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The temperature and melting load of glass melting furnaces. W. Trier, *Cent Glass Ceram Res Inst Bull*, **23** (1) 1-4 (1976).

The history of development of the glass melting furnace over the past years has been marked by an increase in melting capacity and a reduction in specific fuel consumption. Due to stricter regulations on dust emissions, the melting temperatures may in fact, have to be reduced. In order to maintain the melting capacities, electrical boosting will gain importance. Introduction of electrical boosting into the refining zone is to be preferred; only in the case of furnace having high melting capacities it should be used in the batch area.

Flow properties of clay minerals during phase transformations. A. C. D. Chaklader, *Cent Glass Ceram Res Inst Bull*, **23** (1) 5-14 (1976).

Transformation plasticity of illite and kaolinite was studied under isothermal conditions and at a constant heating rate. It was observed that although reasonable plasticity existed during the dehydroxylation reaction of kaolinite, very minimal plasticity was encountered with illite during the same reaction. In both cases — kaolinite and illite, enhanced compaction preceded the exothermic reaction in kaolinite (990°) and endothermic-exothermic reaction in illite (900° – 950°). It is proposed that the transformation of metakaolin to spinel and metakillite to mullite occurs before the reaction temperatures usually encountered in dta plots of these minerals. The exothermic peak in the dta plots is the result of crystallisation of amorphous silica.

History of a research project: glass-ceramics. G. P. Smith, *Cent Glass Ceram Res Inst Bull*, **23** (1) 15-23 (1976).

The history of a research project on glass-ceramics at Corning Glass Works has been elucidated. Out of elaborate presentation of facts six important aspects are illuminated which are considered key to the progress of research work in terms of achievement made by the glass industry at Corning.

Absorption characteristics of Nd^{3+} ion in glasses. A. Singh and P. Nath, *Cent Glass Ceram Res Inst Bull*,

23 (1) 23-30 (1976).

Absorption characteristics of Nd^{3+} ion in ternary aluminoborate glasses having the general composition $15\text{R}_2\text{O}$, 30RO , $10\text{Al}_2\text{O}_3$, $75\text{B}_2\text{O}_3$ and aluminate glasses were studied in the range 300-1100 $\text{m}\mu$ wave length. Energy levels for the peaks were assigned. With increasing ionic radii of the alkali and alkaline earth ions, the molar extinction coefficient at various peaks in the visible range except at 585 $\text{m}\mu$ increased. At 585 $\text{m}\mu$ extinction coefficient increased in the order $\text{Li} < \text{K} < \text{Na}$ and $\text{Ba} < \text{Sr}$. The absorption peaks in aluminate glass are at longer wave lengths than those in alkali and alkaline earth aluminoborate glasses.

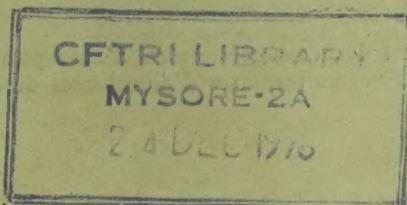
Investigation on some new sources of raw materials for glass industry: Silica deposits from Kalyasota-Maheshnadi of Purulia District, West Bengal. S. K. Basu, S. K. Gupta and S. N. Prasad, *Cent Glass Ceram Res Inst Bull*, **23** (1) 30-32 (1976).

Five samples of silica deposits from Kalyasota-Maheshnadi area of Purulia district in West Bengal were evaluated for their potentiality in glass making. One sample on beneficiation conformed to grade II of IS: 488-1963 while three other samples (T_1 , T_4 and KgD_5) did not. Their iron contents, however, are within the range of this standard. The sand stones may be used in the manufacture of ceramic articles after grinding to 6-5 mesh IS sieve.

Thermal expansion behaviour of some sulphate containing lead glasses. M. D. Karkhanavala and B. S. Shukla, *Cent Glass Ceram Res Inst Bull*, **23** (1) 33-37 (1976).

With glasses of different types of network formers, the Yatsimirskii concept of thermochemical ionic radius leads to a reasonably good prediction of the thermal expansion behaviour. The values of α obtained are in good agreement with that given in the literature on this subject.

The dilatometric softening temperature of the glasses decrease by adding Na_2O or Na_2SO_4 but increase by adding SO_3 . The substitution of Na_2O for PbO ; B_2O_3 for SiO_2 and SiO_2 for SO_3 decreases the softening temperature. For a fixed mole per cent substitution, the decrease in softening temperature is maximum when B_2O_3 is substituted for SiO_2 and minimum when SiO_2 is substituted for SO_3 .



La température et la tirée des fours de verrerie.
W. Trier, *Cent Glass Ceram Res Inst Bull*, **23** (1) 1-4 (1976).

L'histoire du développement de four de fusion de verre au cours de ces dernières années a connu une augmentation de capacité de fusion et un abaissement de consommation du combustible. En effet, on doit abaisser les températures de fusion due aux lois rigoureuses réglant le dégagement de poussière. Comme on voudrait garder les capacités de fusion l'utilisation de chauffage électrique d'appoint va gagner de l'importance. L'application en est préférable dans la zone d'affinage. Le chauffage électrique d'appoint doit être utiliser seulement dans la zone d'enfournement de fours ayant de hautes capacités de fusion.

Propriétés d'écoulement de minéraux d'argile au cours de la transformation de phases. A. C. D. Chaklader, *Cent Glass Ceram Res Inst Bull*, **23** (1) 5-14 (1976).

L'auteur examine la transformation de plasticité d'illite et de kaolinite dans des conditions isothermiques et à une vitesse de chauffage constante. Il constate que bien qu'il existe une plasticité modérée lors de la réaction de déhydroxylation de kaolinite, on obtient une plasticité très faible dans l'illite au cours de la même réaction. Dans les deux cas, la kaolinite et l'illite augmentent la compaction ce qui est précédé par la réaction exothermique dans la kaolinite (990°) et endothermique-exothermique dans l'illite (900° - 950°). L'auteur suggère que la transformation, de métakaolin en spinelle et de meta-illite en mullite, se produise avant d'atteindre les températures de réaction dans le graphique de l'a. t.d. de ces minéraux. Le crochet exothermique obtenu dans le graphique de l'a. t.d. est due à la cristallisation de la silice amorphe.

Histoire d'un plan de recherche: verre-céramique.
G. P. Smith, *Cent Glass Ceram Res Inst Bull*, **23** (1) 15-23 (1976).

L'auteur met au jour l'histoire d'un plan de recherche du Corning Glass Works sur le verre-céramique. Dans cet article, il présente en détail des renseignements parmi lesquels il discute de six aspects importants qu'il en faut pour le progrès de la recherche tenant compte des succès accomplis par l'industrie verrière.

Caractéristiques d'absorption du ion Nd^{3+} dans les verres. A Singh et P. Nath, *Cent Glass Ceram Res Inst Bull*, **23** (1) 23-30 (1976).

Les auteurs étudient les caractéristiques d'absorption du ion Nd^{3+} dans les verres ternaires d'aluminates dont

la composition générale est $15R_2O$, $30RO$, $10Al_2O_3$, $75B_2O_3$ ainsi que dans les verres d'aluminates dans le domaine de la longueur d'onde de 300 à 100 $m\mu$. On donne les niveaux d'énergie pour les crochets. Avec l'accroissement des rayons ioniques de l'alcali et des ions des terres alcalines, le coefficient d'extinction molaire dans divers crochets s'accroît dans l'intervalle du gamme visible, sauf à 585 $m\mu$. A 585 $m\mu$, le coefficient d'extinction s'accroît dans l'ordre de $Li < K < Na$ et $Ba < Sr$. Les crochets d'absorption dans les verres d'aluminates, sont dans la longueur d'onde plus grande que ceux dans les verres d'alcali et dans les verres d'aluminate de terre alcaline.

Récherches sur quelques provenances nouvelles de matières premières pour l'industrie de verre. Cinquième Partie: Le gisement de silice de Kalyasota-Maheshnadi, Purulia, Bengale occidental.
S. K. Basu, S. K. Gupta et S. N. Prasad, *Cent Glass Ceram Res Inst Bull*, **23** (1) 30-32 (1976).

L'étude a porté sur cinq échantillons provenant du dépôt de silice, sous forme de grès, de la région de Kalyasota-Maheshnadi, située au Purulia dans la province du Bengale occidental en vue de déterminer leur possibilité d'utilisation dans l'industrie de verre. Après l'enrichissement, l'un de ces échantillons se conforme à la norme indienne (Grade II IS: 488-1963), et les trois échantillons (T_1 , T_4 et KgD_5) ne s'y conforme pas bien que leurs teneurs en fer soient satisfaisantes à la norme sus-dite. Après broyage et tamisage (tamis IS de 6 à 5 maille), il serait possible d'utiliser ce grès pour la fabrication des produits céramiques.

Caractéristiques de dilatation thermique de quelques verres au plomb contenant de sulfates. M. D. Karkhanawala et B. S. Shukla, *Cent Glass Ceram Res Inst Bull*, **23** (1) 33-37 (1976).

La notion Yatsimirshii du rayon d'ion thermochimique conduit à prévoir assez correctement les caractéristiques de dilatation thermique dans les verres contenant de types différents de formateurs de réseaux. Les valeurs de α sont en accord avec celles données dans la littérature sur ce sujet.

La température de ramolissement pendant l'essai dilatométrique de verre décroît par l'addition de Na_2O ou de Na_2SO_4 mais, elle augmente par l'addition de SO_3 . La substitution de Na_2O par PbO , B_2O_3 par SiO_2 et SiO_2 par SO_3 décroît la température de ramolissement. Pour un mole pour cent fixe de substitution, le décroissement de la température de ramolissement est maximale lorsque B_2O_3 est remplacé par SiO_2 et minimale lorsque SiO_2 est remplacé par SO_3 .

Die Temperatur und Schmelzleistung von Glasschmelzöfen. W. Trier, *Cent Glass Ceram Res Inst Bull*, **23** (1) 1-4 (1976).

Die Geschichte der Entwicklung vom Glasschmelzofen während der letzten Jahrzehnten ist durch eine Erhöhung in Schmelzkapazität und eine Verminderung in Spezifischerbrennstoffverbrauch gekennzeichnet. Infolge der stärkeren Kontrollierung über Staubemissionen sollen in der Tat die Schmelztemperaturen vermindert werden. Um die Schmelzkapazität aufrechtzuhalten, wird die Elektrische-Zusatzheizung wichtig. Einleitung von elektrischem Zusatz in der Läuterungszone wird bevorzugt werden; nur im Falle der Ofen mit höherer Schmelzkapazität soll es im Glassatzraum benutzt werden.

Fließverhalten von Tönmineralien während Phasenumwandlungen. A. C. D. Chaklader, *Cent Glass Ceram Res Inst Bull*, **23** (1) 5-14 (1976).

Umwandlungsplastizität von Illit und Kaolinit wurde unter isothermischen Zustände und bei einer konstanten Erhitzungsgeschwindigkeit untersucht. Es wurde beobachtet, dass obwohl einen gewissen Grad der Plastizität während der Dehydroxylierungsreaktion von Kaolinit existierte, mit Illit sehr geringe Plastizität während derselben Reaktion angetroffen wurde. In den beiden Fällen, Kaolinit und Illit, hatte die erhöhte Verdichtung den Vorrang von der exothermischen Reaktion in Kaolinit (990°) und der endothermisch-exothermischen Reaktion in Illit (900°-950°). Es wird vorgeschlagen, dass die Umwandlung von Metakaolin zu Spinell und Metallit zu Mullit, vor der Reaktionstemperaturen angetroffen in den DTA-Kurven von diesen Mineralien stattfindet. Die exothermische Spitze in den DTA-Kurven ist das Ergebnis der Kristallisation von amorphem Silika.

Geschichte eines Forschungsprojekts: Glas-Keramik. G. P. Smith, *Cent Glass Ceram Res Inst Bull*, **23** (1) 15-23 (1976).

Die Geschichte einer Forschungsarbeit über Glas-Keramik bei der Corning Glasfabrik ist in der vorliegenden Arbeit gegeben. Aus der ausgearbeiteten Darstellung sind sechs wichtige Aspekte, die als Fortschrittsschlüssel der Forschungsarbeit in der Sprache der Leistungen erreicht von der Glasindustrie betrachtet werden, in der vorliegenden Arbeit ausgeleuchtet.

Absorptionseigenschaften vom Nd^{3+} Ion in Gläser. A. Singh und P. Nath, *Cent Glass Ceram Res Inst Bull*, **23** (1) 23-30 (1976).

Absorptionseigenschaften vom Nd^{3+} -Ion in Ternär Aluminoborat Gläser mit allgemeiner Zusammensetzung $15 \text{R}_2\text{O}$, 30RO , $10 \text{Al}_2\text{O}_3$, $75 \text{B}_2\text{O}_3$ und Aluminatgläser wurden im Bereich 300-1100 $\text{m}\mu$ Wellenlänge untersucht. Energieniveau für die Kurvenscheitelpunkte wurden zugeordnet. Mit zunehmender ionischen Halbmesser von Alkali und Erdalkali Ionen erhöhte der Molarextinktionskoeffizient bei verschiedenen Kurvenscheitelpunkte im sichtbaren Bereich ausser bei 585 $\text{m}\mu$. Bei 585 $\text{m}\mu$ erhöhte der Extinktionskoeffizient in Ordnung $\text{Li} < \text{K} < \text{Na}$ und $\text{Ba} < \text{Sr}$. Die Absorptionskurvenscheitelpunkte in Aluminatgläser liegen im Bereich der längeren Wellenlänge als die Wellenlänge bei Alkali und Erdalkali Aluminoboratgläser.

Untersuchungen an einige neue Quellen von Rohstoffen für Glasindustrie: Silika Ablagerungen aus Kalyasota-Maheshnadi von Purulia Bezirk, West Bengalen. S. K. Basu, S. K. Gupta und S. N. Prasad, *Cent Glass Ceram Res Inst Bull*, **23** (1) 30-32 (1976).

Fünf Proben von Silika Ablagerungen aus dem Kalyasota-Maheshnadi Gegend von Purulia Bezirk in West Bengalen wurden für ihre Eignung in Herstellung von Glas abgeschätzt. Eine Probe nach der Aufbereitung entsprach Grad II von IS: 488-1963, was drei andere Proben (T_3 , T_4 und KgD_5) nicht entsprachen. Ihre Eisengehalts jedoch lagen innerhalb des gegebene Bereiches dieser Norm. Der Sandstein kann in der Herstellung von keramischen Waren nach Zermahlen bis 6-5 Siebfeinheit von IS Siebe benutzt werden.

Wärmeausdehnungsverhalten von einigen sulphathaltigen Bleigläser. M. D. Karkhanavala und B. S. Shukla, *Cent Glass Ceram Res Inst Bull*, **23** (1) 33-37 (1976).

Mit Gläsern von verschiedenen Sorten von Netzwerkbildner führt der Yatsimirskii-Begriff von thermochemischen ionischen Halbmesser zu einer ziemlich guten Voraussage des Wärmeausdehnungsverhalten. Die ausgerechneten α -Werte sind in guter Übereinstimmung mit denen, die in der Literatur über dieses Thema angegeben sind.

Die dilatometrische Erweichungstemperatur der Gläser nahm mit Zugabe von Na_2O oder Na_2SO_4 ab, aber steigert mit Zugabe von SO_3 . Die Ersetzung von PbO durch Na_2O ; SiO_2 durch B_2O_3 und SO_3 durch SiO_2 vermindert die Erweichungstemperatur. Für eine konstante Molprozent-Ersetzung ist die Verminderung in Erweichungstemperatur maximum wenn SiO_2 durch B_2O_3 ersetzt ist und minimum wenn SO_3 durch SiO_2 ersetzt ist.

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THE TEMPERATURE AND MELTING LOAD OF GLASS MELTING FURNACES

W. TRIER*

Introduction

When considering the development of the glass melting furnace over the last 30 years, it is noticeable that the basic concept, going back to F. Siemens, has not changed at all. The specific melting load and the lifetime of the installations have considerably increased, thus greatly reducing the specific heat consumption at the same time. The melting capacity has been increased from 1 tonne of glass/m² 24 hours to more than 3 tonnes of glass/m² 24 hours. In production of glass containers the heat consumption has, in fact, been reduced from 3000 kcal/kg to 1400 kcal/kg and below. Particularly, noticeable is the extension of the furnace-lifetime from one year to five years and more. How did this increase in performance come about and what further developments can be expected in the years to come?

Development during the past years

The main reasons for the above mentioned development are primarily due to two influences. Firstly, the continuous improvement of the refractory materials and, secondly, the improvement of the firing systems. The utilisation of fusion-cast blocks with carefully graded properties for the various highly corrosive areas of the furnace, good quality basic brick for the regenerative chambers and silica bricks for the crown have to be mentioned in the first instance. Hand in hand with the refractory materials the firing systems have improved decisively. Ballast-rich generator gas has been substituted by oil or natural gas and the flame development and position improved by underport firing.

The better refractory materials in combination with tighter tolerances for the blocks and refinement of the design made it possible to insulate the melting furnace, particularly the superstructure, also the melting section. The regenerative chambers were enlarged. Both these steps resulted in a considerable decrease in fuel consumption. A further factor has been a better control of the glass currents, especially through restriction of the return currents from the conditioning zone.

Due to these described measures, melting temperatures have increased steadily. Whereas in the past, temperatures around 1480° were the upper limit, nowadays, 1580° to 1600° are normal operating temperatures. These higher melting temperatures permitted the melting load to be increased considerably. Fig 1 shows the empirical correlations between melting temperature, melting capacity, fuel

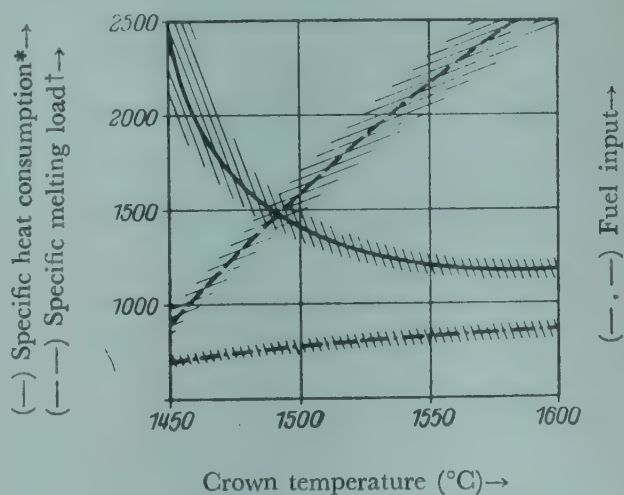


Fig 1
Specific melting load, specific heat consumption and fuel input as a function of the crown temperature
* (kcal/kg glass); † (kg glass/m²d)

*Deutsche Glastechnische Gesellschaft, 6, Frankfurt am Main 1, West Germany

consumption and fuel input as they appear. They can also be obtained mathematically.

Quite remarkable is the almost linear correlation between melting temperature and maximum permissible melting capacity for a given glass quality. In order to be able to utilise the increased melting load, the fuel intake of the furnaces has to be increased. The increase in the amount of fuel is a little less than the increase in the melting capacity, because the thermodynamic efficiency of the unit increases with the temperature and the specific heat consumption decreases. However, these correlations are only valid when the heating system is sufficiently efficient to be able to use the additional fuel and when by enlargement of the chambers their efficiency can be maintained, if possible, increased.

For a given furnace with specified chambers there will be deviations from the illustration (Fig 1) when the melting temperature is increased. Fundamentally, every melting tank will follow the relationship (Fig 2) between the specific melting capacity and the specific heat consumption. With increased load the heat consumption declines, reaches a minimum and then increases again. At a position left to the minimum, the reserves of the furnace heating system are not being fully utilised. On increasing the melting temperature of such a unit, in

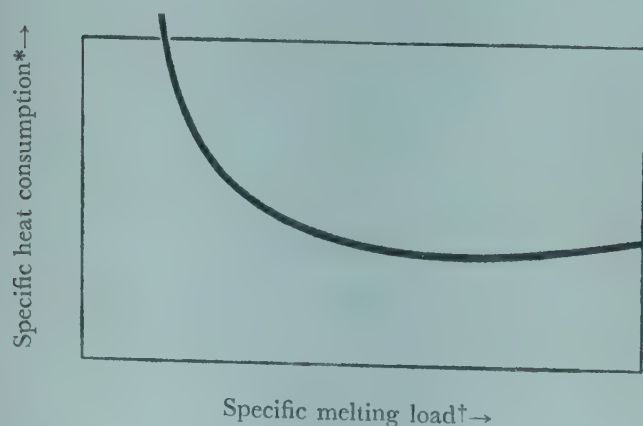


Fig 2
Thermodynamic behaviour of glass tank furnaces
* (kcal/kg glass) † (kg glass/m²d)

principle, the correlations (Fig 1) will become valid, even though, with a decline of the chamber efficiency (chamber volume stays constant, waste gas volume increases) the increase of the melting capacity is somewhat lower. However, if the heating system is positioned to the right of the minimum (Fig 2) then a temperature increase brings about a small increase in melting capacity, but raises the specific and absolute fuel consumption.

Developments in the next few years

First of all, it is to be expected that in spite of many patents and new ideas the conventional design and operation of the glass melting furnaces will be maintained.

Secondly, the question arises whether the melting temperature will be further increased and whether the temperature of 1600° for soda-lime glass will be surpassed. This question cannot be answered easily. An increase in the melting temperature above 1600° requires a move away from the silica arch and the use of more expensive special bricks. In principle, this is possible.

From the heating point of view, an increase in the melting temperature is also possible, especially if the use of combustion air enriched with oxygen, is taken into consideration. A reduction in the N₂-ballast can thus be achieved and an enlargement of the regenerative chambers possibly avoided. However, even without oxygen, but with larger chambers, an increase in melting capacity can be achieved, particularly when specially prepared batch (compacted or pelletised) is used.

Each increase in melting temperature is accompanied by an increase in vapourisation of alkalis from the glass surface, with the result of correspondingly higher dust emissions. The over-proportionally large increase in vapourisation and resulting emissions at temperatures above 1550°, as well as the intensifying pollution directives of the various countries, will not allow the temperature to be increased further, but will in fact lead to a possible decrease. In order to

maintain the melting capacities, electrical boosting will be used more and more.

As far as the area of introduction is concerned, *ie*, melting zone or refining zone, the thermodynamic effect of an electric boosting varies. Neglecting the change in the specific heat of the glass, the same energy is required to heat glass from 1400° to 1500° or from 900° to 1000°. However, with regard to the flame heating, the influence of the temperature level is considerable. Because, only a part of the total energy required to melt a given quantity of glass is contributed by electrical boosting, an efficiency of 1 is not feasible, also for the multiple melt, even if additional losses due to the electrode cooling, *etc*, are neglected. The efficiency will improve with increased effectiveness of the electrical boosting in the hot area, because here the losses through the flame heating are at their greatest.

A similar effect is shown when considering the relationship between electrical energy and fuel energy. If only a small quantity of electrical energy is used, the energy input for the boosted melt is larger, thus decreasing the effectiveness of the electrical boosting more than when electrical energy is used on a larger scale. A glass melting tank with electrical boosting must not be considered as two parallel, largely independent, glass melting units, one of which is operated with fuel and the other with electricity. In electrical boosting the glass is only partly heated by electricity, for instance, from 1100° to 1200°. The rest, below and above, is done by fuel. In the work of H. Gneist, H. Hohmann and G. Walter¹, this relationship is confirmed by experiment.

By indirect influences, for instance, by effecting the glass currents, the efficiency of the boosting can increase above 1. This, however, has nothing to do with direct energy correlations. These illustrated relationships have been calculated for certain parameter constellations using a mathematical model². The results are shown in Fig 3.

The intensity of the flame heating up to regions

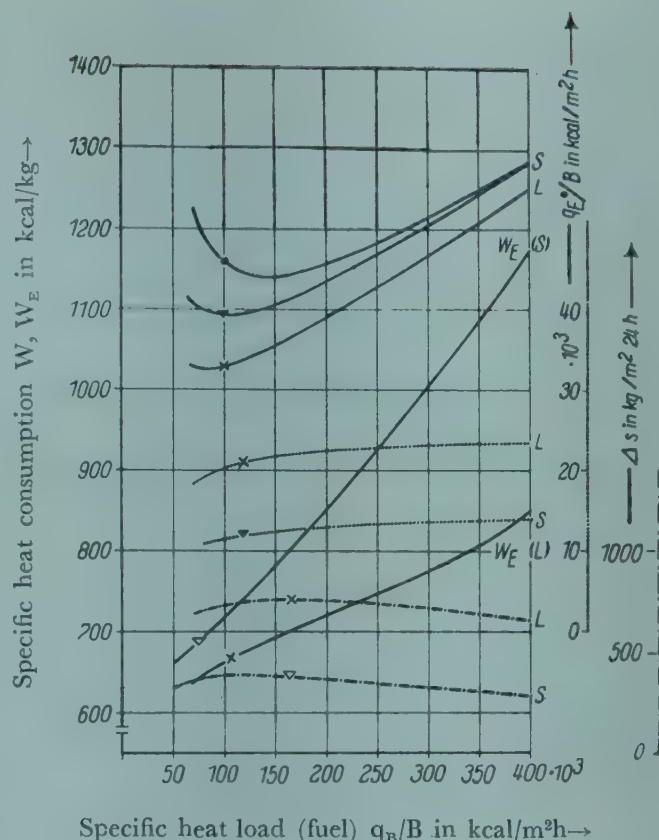


Fig 3
Influence of electrical boosting (EZH) on various thermodynamic data of a melting furnace: ●—without electrical boosting (EZH); ▼—electrical boosting in the batch melting area; ×—electrical boosting in the batch free area; Δs —additional melting capacity with electrical boosting; q_E^*/B —specific electrical heat load (kcal/m²h); W —specific heat consumption (fuel) [kcal/kg glass]; W_E —specific heat consumption (electricity) [kcal/kg glass]; q_B/B —specific heat load (fuel) [kcal/m²h]

of very high specific energy densities is taken as the abscissa. The ordinate corresponds to the specific heat consumption, on the one hand, referring to the heat introduced by the fuel and, on the other hand, taking into consideration the use of electrothermal energy to achieve a corresponding increase in melting capacity. The two curves involving the introduction of electrical energy are divided into $W_E(L)$ and $W_E(S)$. The curves thus refer to the introduction of electrical energy in the melting area. It is immediately obvious that the curve for the specific heat consumption where electrical heating is introduced in the refining zone lies clearly lower and in the neighbourhood of the theoretical heat consumption, while the curve corres-

ponding to the introduction of the electrical energy in the melting zone shows a much steeper slope. Both curves apply only to one or the other case, a combination of the two has not been taken into consideration in the mathematical model. As additional ordinates the specific electrical capacity in kcal/m²h and the increase in melting capacity in kg/m² 24 hours are also given. The total electrical capacity is altered somewhat here, because the areas between batch blanket and the free glass batch are also shifted, the effect is, however, not very large. It is very clearly demonstrated that the greater the furnace is loaded and the larger the proportion of flame energy to electrical heat becomes, the more uneconomical the use of electricity becomes. The reason for this, as already mentioned, is that only a part of the introduced energy is supplied by electricity, while a much larger proportion has to be covered by the flames, thereby increasing the thermal losses correspondingly. If one considers, for instance, a flame heated furnace and introduces electrical boosting, the first kw of electrical energy are more poorly utilised than in the case of increased electrical capacity, where there is a larger contribution to the total heat requirement.

The results of the correlations (Fig 3) are based on the equation² (11a). The calculation itself was improved. While the specific fuel energy² conditions in the melting and refining areas qB_1 and qB_2 were kept constant, the change in the total energy input, [$^qB_1 \cdot L_1 + (L_2 - L_1) \cdot ^qB_2$] due to alteration of the batch blanket length (L_1), however, neglected, this influence was taken into account in the results (Fig 3). Because when introducing electrical boosting

the glass temperature in the throat rises, the final temperature of the glass in the refining area with pure flame heating was assumed to be 1500°, with flame heating combined with electrical boosting 1550°, and accordingly these are introduced into the equation. The other data (parameter values are shown in the diagrams) correspond to the data¹. The approximate value ψ which takes into consideration the intensity of the glass flow from the refining zone into the melting zone, was kept constant in the calculation. This procedure represents a simplification, the effect of which cannot be calculated at the present time. It is certain that electrical boosting changes the glass flow. Electrical boosting in the melting zone will reduce the return current system under the batch area, whereas, a boosting in the refining zone will increase it.

Summary

The development of the glass melting furnace over the past years, favoured by better refractory materials and by a noticeable increase in melting temperature, has been marked by an increase in melting capacity and a reduction in specific fuel consumption. A further increase of the melting temperature over the next few years is not to be reckoned with. Due to stricter regulations on dust emissions, the melting temperatures may in fact, have to be reduced. In order to maintain the melting capacities, electrical boosting will gain importance. Introduction of electrical boosting into the refining zone is to be preferred; only in the case of furnaces having high melting capacities it should be used in the batch area.

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FLOW PROPERTIES OF CLAY MINERALS DURING PHASE TRANSFORMATIONS

A. C. D. CHAKLADER*

Introduction

The most widely used raw materials in ceramic industries are based on clay minerals. Although there are several mineralogical constituents in so called clays, the principal minerals are kaolinite, illite and montmorillonite. Most of the refractory clays such as china clay, fire-clay, and ball clay are kaolinite based and the major clay mineral in most common clays is illite. The mineralogy of kaolinite and its transformation behaviour during heating have been extensively investigated, and to a lesser extent the mineralogy of illite has also been studied. The effect of heat on kaolinite¹ and illite³ under constant heating rate can be summarised as follows:

Kaolinite: (a) An endothermic reaction due to dehydration at 150° to 250° depending upon crystallinity; (b) an endothermic reaction due to dehydroxylation at 550° to 600°; (c) an exothermic reaction at 950° to 1000°, generally assigned to the formation of a Al-Si spinel type structure from kaolinite. Also sometimes referred to as the formation of γ -Al₂O₃ at this stage; and (d) above 1100° formation of mullite is generally encountered. Some workers reported² an exothermic reaction associated with the formation of mullite.

Illite: (a) A moderately-sized low-temperature endothermic effect with the peak at about 130° due to dehydration; (b) the main endothermic peak at ~550° to 575° due to dehydroxylation reaction; and (c) occasionally an endothermic-exothermic peak in the neighbourhood of 900° to 950°.

Because of very poor crystallinity of illite, the crystal phase relationships in this transformation sequence are not accurately known. Moreover, the large impurity substitution (Mg²⁺ and Fe in Al³⁺ locations) always associated with this mineral and presence of other minerals, such as montmorillonite, mica, *etc*, in illite make it more difficult to study its transformation behaviour. On the other hand, the appearance and disappearance of crystal phases in the transformation sequence of kaolinite to mullite have been thoroughly investigated and reasonably understood¹. This is in spite of the fact that controversy still exists about the nature of the cubic phase, which emerges from metakaolin⁴.

In this paper, the flow behaviour of kaolinite and illite during their phase change on heating has been reported. The purpose of this study is to determine the nature of transformation plasticity associated with the phase changes in clay minerals. Also the enhanced plasticity associated with phase changes in clay minerals may shed some more light into the physical and chemical nature of the transformation sequence. Furthermore, for any future application of transformation plasticity in industrial practices, it will be helpful if the mechanism involved in this phenomenon, *ie*, transformation plasticity is understood.

Experimental Procedure

Materials: Both minerals, kaolinite and illite, supplied by Ward's Natural Science Establishment, Inc, Rochester, NY; are a Georgia kaolin and a Fithian (Illinois) illite, respectively. The kaolinite mineral appeared to be well-formed hexagonal platelets (Fig 1a) having

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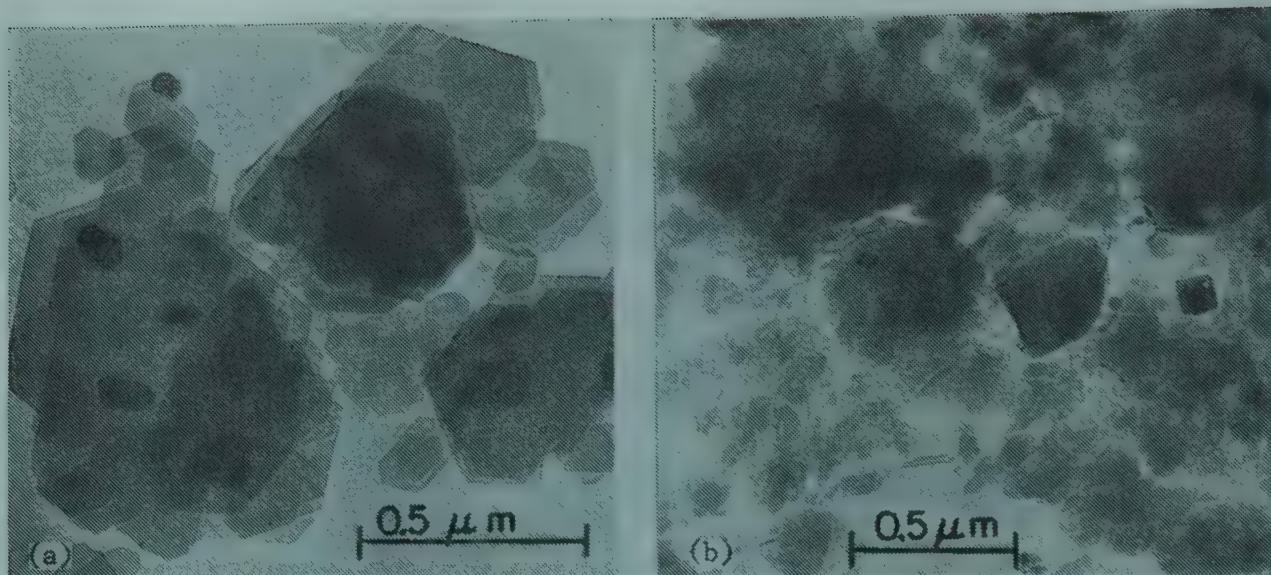


Fig 1
Transmission electronphotomicrograph of: (a) kaolinite and (b) illite.

the average width of $0.5\ \mu\text{m}$. The illite, on the other hand appeared to be very fine platelets of $\sim 0.1\ \mu\text{m}$ (Fig 1b) and poorly defined.

Hot-pressing equipment: The details of the hot-pressing equipment have been published in several papers^{5,9}. The hot-pressing apparatus is essentially an inductively heated graphite die (2 cm inside dia), which acted as the susceptor. The Phillips 12 kw induction unit has a temperature controller attached with it. The pressure was applied through a hydraulic jack connected with a gas cylinder through a pressure-multiplier. With this arrangement a constant pressure can be maintained on the system even if there is a considerable shrinkage due to mass-loss during dehydroxylation. The linear dimensional change was measured by an inductive displacement transducer connected to a strain gauge bridge and a strip chart recorder and also directly by a dial gauge indicator (sensitivity $0.00025\ \text{cm}$) connected in tandem with the transducer. Experiments were carried out both under isothermal conditions and at a constant heating rate. For compaction experiments under a constant heating rate, the pressure was applied on the specimen and maintained till a mechanical equilibrium was attained in the system and then the power was applied

for heating. For tests under isothermal conditions, the specimen was precompacted at a pressure to be later used for isothermal compaction experiments and the pressure was released. The specimen was heated to the desired temperature and maintained for about three minutes for equilibration before the pressure was applied. The compaction was determined as a function of time and the pressure was released to determine the elastic spring-back which was subtracted from the total shrinkage to evaluate the true compaction during the transformation. The experimental procedure is schematically represented (Fig 2).

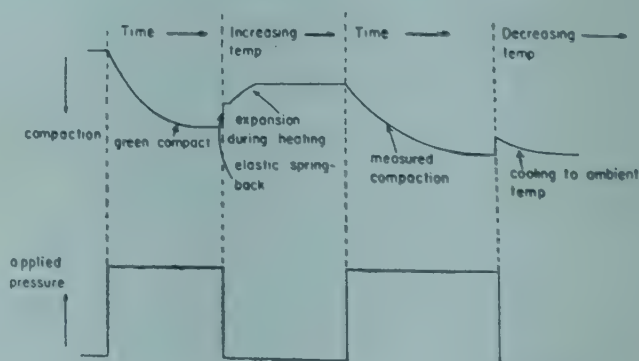


Fig 2
Schematic representation of hot-pressing under isothermal conditions

Results

Compaction at a constant heating rate: Compaction curves at a constant heating rate under 2000 psi for both kaolinite and illite as a function of temperature are shown (Fig 3). A compaction curve of a Tennessee ball clay is also included for comparison. The most important feature in this figure is that the compaction characteristics of kaolinitic clays (including ball clay) are different from that of the illitic clay. There are three characteristic regions of enhanced compaction in kaolinite, 550° to 650°, 835° to 980° and above 1160°. The dta plots for these minerals are also included (Fig 3), to indicate the correspondence of the well-known phase transformation characteristics of the minerals. The following observations can be made:

Kaolinite: (i) There is no compaction below 550°; (ii) during the dehydroxylation reaction at 550° to 650° there is an enhanced compaction; (iii) the second enhanced compaction, starting at ~835° and finishing at ~980°, is prior to the first exothermic reaction in the dta plot; (iv) subsequent enhanced compaction (which may be a two-stage process) above 1160°, has no identifiable dta reaction; and (v) in some dta plots, a very small exothermic peak at ~1300° was obtained.

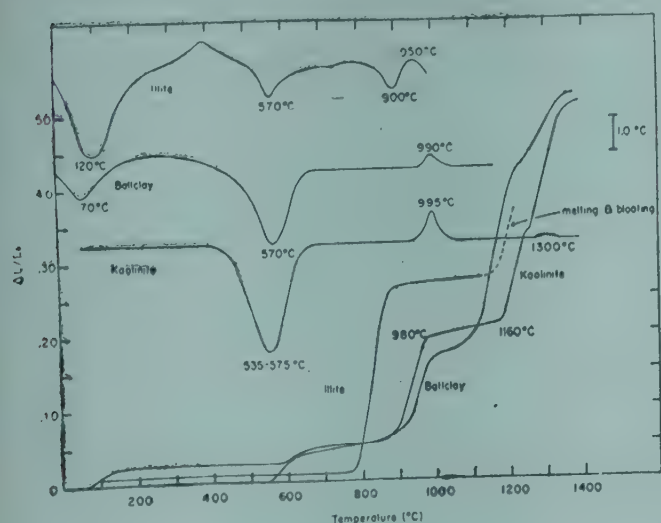


Fig 3

Compaction of three clay minerals as a function of temperature under 2000 psi. Dta plots are included for comparison

The Tennessee ball clay has a very similar compaction behaviour to that of the Georgia kaolinite, with an additional small enhanced compaction with the endothermic reaction (dehydration) at ~100°. The final compaction started at 1075° and continued up to 1400°, the maximum temperature used.

Illite: (i) The first large endothermic peak in the dta plot has a small but definite compaction (~1 per cent of the total compaction) associated with it; (ii) the second large endothermic peak at ~570° has no detectable compaction accompanied with it; instead, the enhanced compaction started at 760° and continued till 900°; and (iii) no enhanced compaction was apparent with the endothermic-exothermic reaction at 900° to 950°. On the other hand, additional compaction was encountered at 1140° due to melting and bloating.

It is significant to note that in all cases, the enhanced compaction associated with the exothermic reaction in the temperature region 950° to 1000°, appears to precede the reaction. Lack of any detectable compaction during the dehydroxylation reaction of illite (~570°) is also important in that it may be indicative of absence of structural disruption in the system, which may be an essential criterion of transformation plasticity.

Isothermal conditions: Isothermal compaction experiments were carried out in the temperature regions where enhanced compaction was encountered during heating at a constant rate, viz, 685° to 940° for illite and 500° to 700°, 900° to 1000° and 1200° to 1300° for kaolinite. Isothermal compaction curves under 2000 psi for illite are shown in Fig 4 and similarly isothermal compaction curves for kaolinite during the metakaolin to spinel transformation under 2000 psi are shown in Fig 5. It should be noted that no enhanced compaction was encountered at 570° (between 500° and 600°) for illite, conforming to our earlier observation about the absence of compaction at this temperature when illite under pressure was heated at a constant heating rate. Another feature of the

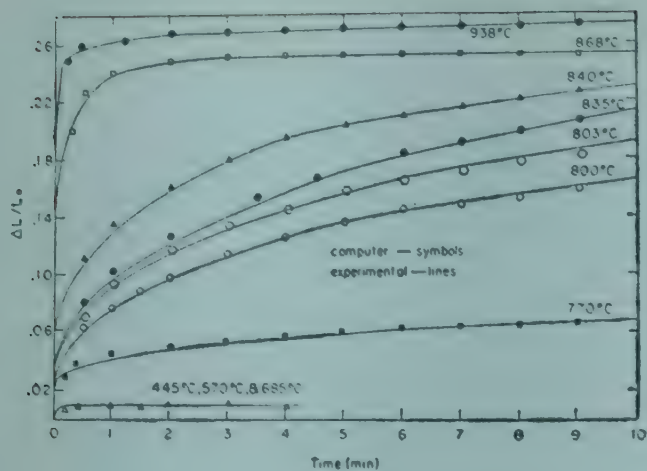


Fig 4
Isothermal compaction curves of illite

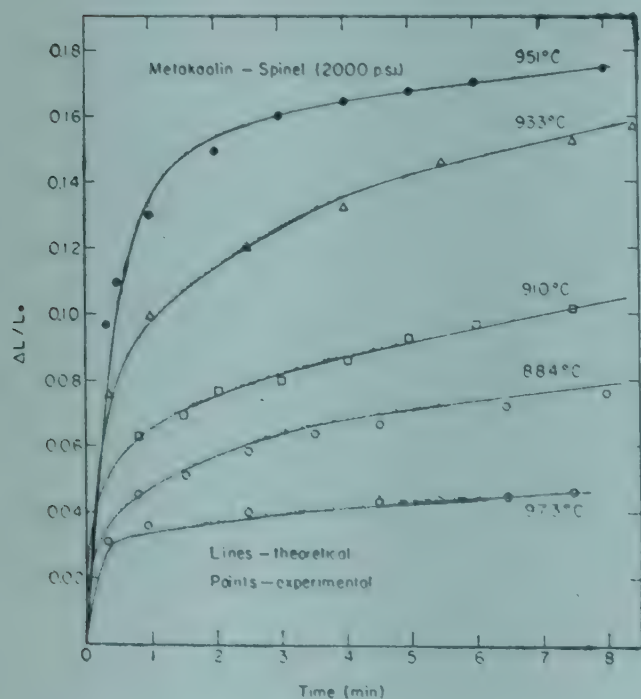


Fig 5
Isothermal compaction curves of kaolinite during metakaolin to spinel transformation

curves of illite is that the total compaction, $(\Delta L/L_0)_{\max}$ increased with increasing temperature, although the shape of the curve at 938° (or, 868°) was different from the curves obtained in the temperature range 800° to 840° (Fig 4). On the other hand, for kaolinite, the total compaction, $(\Delta L/L_0)_{\max}$ first increased (885° to 951°) and then decreased at a higher temperature of 973° (Fig 5). Similar

behaviour was also encountered with kaolinite during kaolin to metakaolin transformation (500° to 700°).

Discussion

Several equations are available to treat isothermal compaction data of solids obtained under a constant pressure. P. Murray, D. T. Livey and J. Williams⁶ derived the following equation to interpret the hot-pressing data of viscous solids (where, D is the relative density):

$$\frac{dD}{dt} = \frac{3\sigma}{4\eta} (1-D) \quad \dots (1)$$

which on integration yields,

$$-\ln (1-D) = \frac{3\sigma t}{4\eta} - \ln (1-D_0) \quad \dots (2)$$

with the boundary condition that at $t=0$, $D=D_0$, the initial bulk density of the compact. σ is the applied stress and η is the viscosity coefficient which is temperature dependent.

An equation identical in form to equation (1) was also derived by R. C. Rossi and R. M. Fulrath⁷, which is based on Nabarr-Herring creep mechanism of deformation during hot-pressing:

$$\frac{dD}{dt} = \frac{40 D_1 \Omega b \sigma}{K T d^2} (1-D) \quad \dots (3)$$

where, D_1 is the diffusion coefficients, Ω is the vacancy volume, b is a stress intensity factor, K is the Boltzmann constant and T is the temperature in °K. Under hot-pressing conditions, the strain rate $\dot{\epsilon}$ is equal to $(1/D) (dD/dt) = -(1/h) (dh/dt)$, where h is the height of the compact. Thus the shrinkage rate of a compact is proportional to the densification rate. A semilog plot of $\Delta L/L_0$ vs time, corresponding to the viscous flow (or, N-H creep) hot-pressing model, produced straight lines in certain region of some of the compaction curves. A log-log plot, corresponding to the liquid phase sintering model⁸ did not fit the data, although a part of these plots became linear. At the

very early stage of reactive hot-pressing, the compaction was very rapid. The data of this region did not fit any models tested so far. As previously reported, the compaction data of both boehmite⁹ and magnesium hydroxide¹⁰ during reactive hot-pressing could be fitted into an equation of the form:

$$\frac{\Delta L}{L_0} = k (1 - Ae^{-\alpha t} - Be^{-\beta t}) \quad \dots (4)$$

where k , A , α , B and β are constants, which can be determined from the experimental plots. It was found also that all compaction curves of both illite and kaolinite under reactive hot-pressing conditions (*ie*, during a phase transformation) could be represented by equation (4). It is apparent that at $t=0$, $\Delta L/L_0=0$, *ie*, $A+B=1$ and $t=\alpha$, $k=(\Delta L/L_0)_{\max}$. The method employed to determine the values of the constants has been reported earlier⁹, and is also summarised below.

If one of the two constants (α or β) is very much greater than the other one, *eg*, $\beta \gg \alpha$, then, when $t \gg 0$, the contribution from the term $Be^{-\beta t}$ to the whole equation is very small and can be neglected. Then taking the derivative of equation (4) and the natural logarithm, the final form (neglecting the second exponential term) of equation is,

$$\ln \left[\frac{d(\Delta L/L_0)}{dt} \right] = -\alpha t + \ln (kA\alpha) \quad \dots (5)$$

The logarithm of the slope of the plot ($\Delta L/L_0$ vs t) at $t > 3$ minutes was plotted as a function of time, the slope of which gave the value of α . Using the experimental value of k and from the intercept ($= \ln kA\alpha$) the value of A was obtained. As $A+B=1$, from this value B was calculated. Then the values of k , A , α , B and experimental values of $\Delta L/L_0$ at different times were substituted in equation (4) and the value β which produced the best fit of experimental data was chosen. The values of the constants (k , A , α , B and β) were then used to obtain a computerised plot of the compaction

curves for comparison with the experimental plots (Figs 4 and 5).

It has been reported previously⁹ that a second order differential equation can be developed from equation (4) which describes the reactive hot-pressing behaviour of solids, especially involving a decomposition reaction. This equation is,

$$\begin{aligned} \frac{d^2\epsilon}{dt} + (\alpha + \beta) \frac{d\epsilon}{dt} + \alpha\beta\epsilon \\ = k(A\alpha + B\beta) \frac{d\sigma}{dt} + k\alpha\beta\sigma \quad \dots (6) \end{aligned}$$

where, $\Delta L/L_0 = \epsilon$.

A viscoelastic model (Fig 6) involving springs and dashpots which has a response similar to equation (6) was developed to interpret the data of boehmite during RHP. The corresponding differential equation for its response is given by:

$$\begin{aligned} \frac{d^2\epsilon}{dt} + \frac{\eta_2(M_1 + M_2) + M_2\eta_1}{\eta_1\eta_2} \frac{d\epsilon}{dt} + \frac{M_1M_2}{\eta_1\eta_2} \epsilon \\ = \frac{1}{\eta_2} \frac{d\sigma}{dt} + \frac{(M_1 + M_2)\sigma}{\eta_1\eta_2} \quad \dots (7) \end{aligned}$$

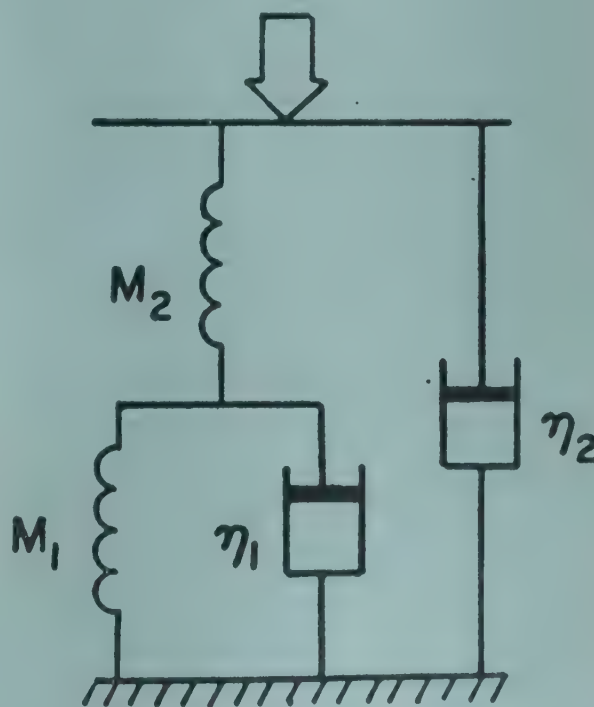


Fig 6

A viscoelastic model to represent the RHP behaviour

Comparing equations (6) and (7), it can be seen that the values of the mechanical parameters η_1 , η_2 , M_1 and M_2 can be calculated with the help of a IBM computer from the

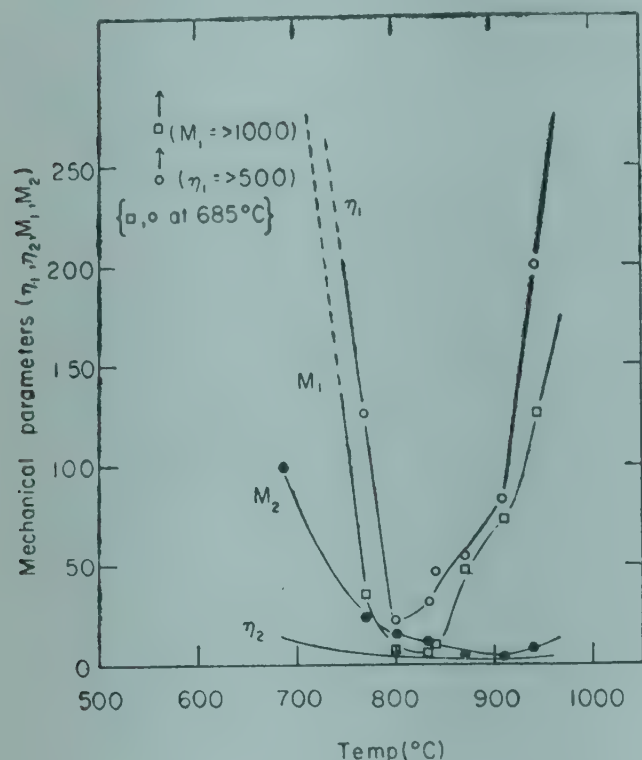


Fig 7

Values of the mechanical parameters η_1 , η_2 , M_1 and M_2 as a function of temperature for illite

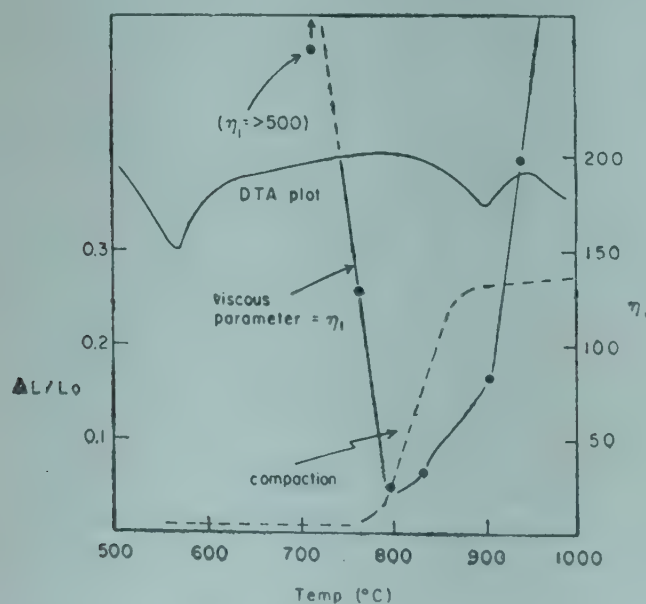


Fig 8

Comparison between η_1 and a compaction curve of illite at a constant heating rate and a dta plot

experimental constants k , A , α , B and β for each compaction curve. The values of the mechanical parameters as a function of temperature for illite are shown in Fig 7. It is quite apparent from this figure that both η_1 and M_1 parameters are very sensitive to temperatures, especially during a phase transformation. The parameters η_2 is insensitive and M_2 is only mildly sensitive to temperature of phase transformation. Both the rigidity (elastic component M_1) and the viscosity (viscous component η_1) were drastically decreased during the phase transformation, reaching a minimum value at about 800°. The dta plot of the illite (Fig 1) does not show any reaction at this temperature. The transformation plasticity appears to precede the endothermic-exothermic reaction encountered in the dta plot (Fig 8), where the viscous parameter η_1 , a dta plot and a compaction curve (with increasing temperature) are shown. The correspondence of the enhanced compaction and the decreasing value of η_1 is significant.

A behaviour similar to that of illite has also been encountered with kaolinite both during the transformation of kaolin to metakaolin and metakaolin to spinel¹¹. Suffice it to mention here that the values of the mechanical parameters η_1 , η_2 , M_1 and M_2 were also calculated from the experimental constants k , A , α , B and β during the transformation sequences from kaolinite to mullite. For the sake of comparison with illite, the variation of the mechanical parameters with temperature during the transformation of metakaolin to spinel is shown in Fig 9. There is a drastic drop in the value of the viscous component η_1 during the critical temperature at $\sim 950^\circ$ (during the transformation). Both the elastic components M_1 and M_2 and the viscous component η_2 are not significantly affected by the transformation. Reduction of the elastic and viscous components will imply higher fluidity in the system, as was manifested by higher compaction (both at a constant heating rate or under isothermal conditions) during the phase transformations in illite and kaolinite.

It can be seen (Figs 7 and 9) that the mechani-

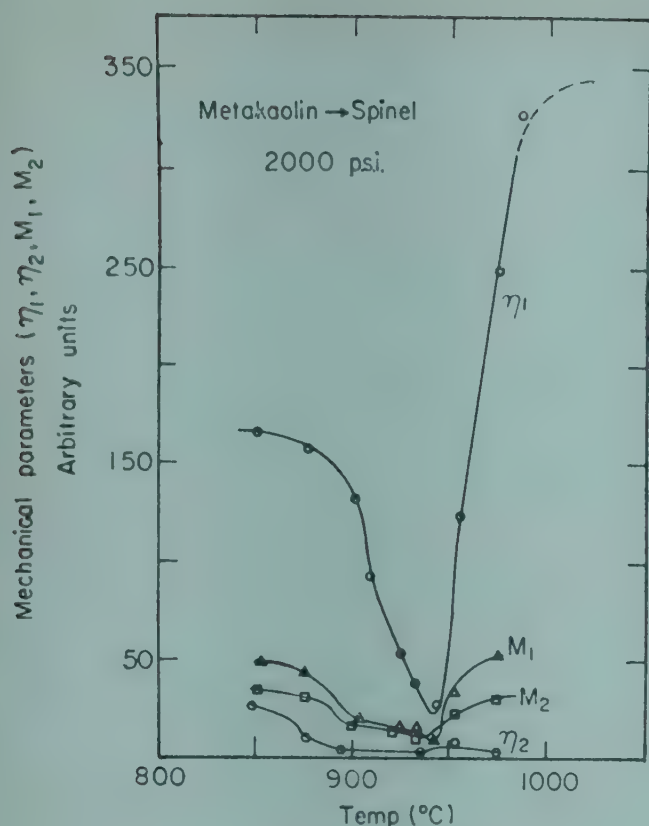


Fig 9

Variation of the mechanical parameters η_1 , η_2 , M_1 and M_2 with temperature during the metakaolin to spinel transformation

cal components η_1 and M_1 (partly) are the only temperature sensitive parameters (*ie*, phase transformation sensitive) in both cases. A similar observation was also made in the case of boehmite⁹ and $\text{Mg}(\text{OH})_2$ ¹⁰ during the dehydroxylation reaction. This suggests that these two components η_1 and M_1 are directly related to the behaviour of the powder or material characteristic during a phase transformation and the overall behaviour can be considered to be viscoelastic.

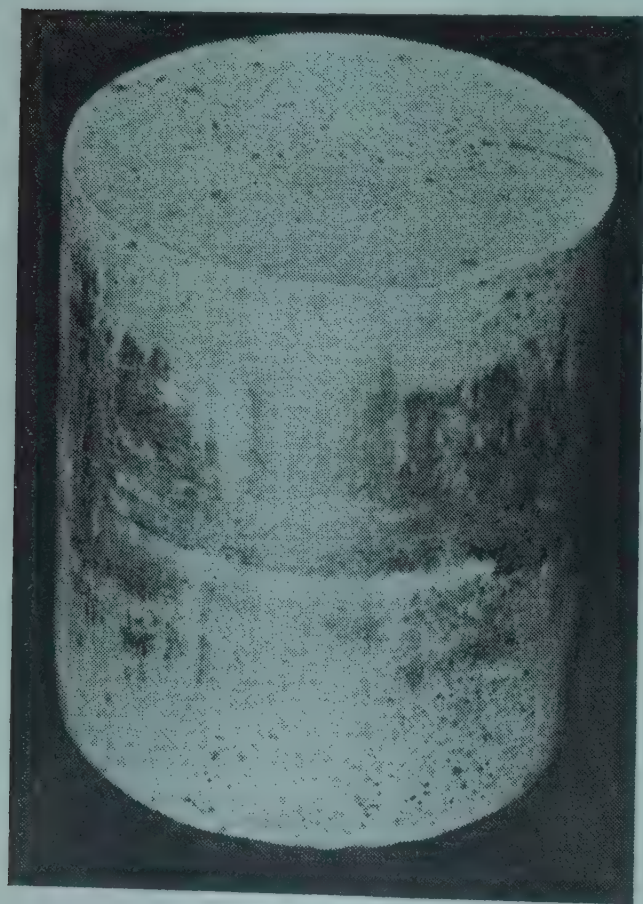
Transformation plasticity vs phase transformation:

Illite: The dta plot of illite indicated that (Fig 1) at 120° (peak temperature) there was dehydration; at ~570° there was dehydroxylation and at 900° to 950° there was an endothermic-exothermic reaction. During the first two reactions there were corresponding weight losses in a TGA plot but no weight change above 900° was encountered. Because of poor crystallinity

and very small particle size ($< 1\mu\text{m}$), X-ray diffraction studies could not detail the structural rearrangement taking place during the phase changes associated with the dehydroxylation reaction at 570° and the endothermic-exothermic reaction at 900° to 950°. If it is considered that illite is a decomposed product of mica as suggested by G. Nagelschmidt¹² and M. L. Jackson¹³, then it is most likely a dioctahedral-double layer mineral¹⁴ (similar to that of pyrophyllite structure with Al^{3+} substitution in tetrahedral locations). Chemical analyses of this mineral show that it contains about SiO_2 50, Al_2O_3 25, Fe_2O_3 5, alkalis 7, MgO 4 and H_2O 9 wt per cent. The equilibrium phase diagrams of Al_2O_3 — SiO_2 — K_2O and Al_2O_3 — SiO_2 — FeO — K_2O indicate that liquid will be formed at as low as 990° and mullite is the only primary crystalline phase present. The structural transformation sequence leading to the formation of mullite from illite is not understood at present but there will be definitely exsolution of SiO_2 molecules from the illite structure, so that Al/Si ratio in illite 1:2 can revert to 3:1 in mullite. Drawing an analogy with kaolinite, it can be assumed that the dehydroxylation of illite at ~570° forming 'metallite' involves very little structural disruption. The reaction leading to the formation of mullite must then be related with the endothermic-exothermic reaction in the dta plot at ~900°. On the other hand, the compaction curve of illite at a constant heating rate (Fig 1) shows that the transformation plasticity begins at ~800°. No corresponding dta reaction peak was encountered at this temperature. It can be speculated that the exsolution of SiO_2 molecules from the illite structure begins at 800° and is a slow and gradual process. The existence of exsolved amorphous silica in the system can give rise to the transformation plasticity encountered between 800° and 900° in this investigation. On the other hand, no enhanced plasticity was encountered between 900° and 950°, where the endothermic-exothermic reaction in the dta plot was obtained. It can only be assumed at this stage that the

endothermic reaction may be the result of final structural rearrangement (or collapse) after the completion of exsolution of silica, which started at 800° and completed at 900°. The endothermic reaction may be due to the effect of crystallisation of silica, as discussed later with respect to the kaolinite transformation.

Although very small transformation plasticity during the dehydration (100° to 200°) and almost no transformation plasticity during the dehydroxylation (500° to 600°) of illite were encountered under 2,000 psi, subsequent experiments at a higher pressure (15,000 to 20,000 psi) indicated some plasticity was present during these two reactions. High density (>85 per cent dense) and strong (>10,000 psi compressive strength) compacts can be made by reactive hot-pressing involving these two reactions. A



A reactive hot-pressed specimen of illite, hot-pressed to 600°

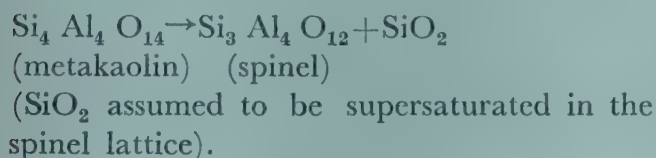
typical example of dense and strong specimen of illite is shown in Fig 10.

Kaolinite: The compaction behaviour of kaolinite both under isothermal conditions and at a constant heating rate indicates¹¹ that there is enhanced compaction during each stage of phase transformation in the consecutive reaction series from kaolinite to mullite. The enhanced compaction associated with the metakaolin to spinel transformation precedes the exothermic peak in a dta plot (Fig 1). It was observed that the densification was encountered as low as 900° although dta traces did not show any reaction until a temperature of 970° to 980° was reached, at which temperature the enhanced compaction (*ie*, TP) was almost over. The analysis of the isothermal compaction data using a viscoelastic model as carried out in this study also indicated that the value of the viscous component η_1 started to decrease below 900°, reaching a minimum value at ~950°. This supports the observation that the enhanced compaction was encountered in the temperature range 900° to 950° at a constant heating rate, *ie*, below the exothermic reaction. This enhanced compaction was completed at ~980°, when also the viscous parameter η_1 reached its maximum value, indicating a drastic reduction in the flow properties of the material.

From the discussion above it is now generally concluded that transformation plasticity exists before the exothermic reaction peak at ~980°. Recent studies by H. J. Percival, J. F. Duncan and P. K. Foster⁴ by IR absorption spectrometry on this system suggests that metakaolin partially decomposes, releasing amorphous $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 before the exothermic reaction peak, but they also implied that the exothermic reaction peak is the result of complete decomposition of metakaolin. P. S. Nicholson and R. M. Fulrath¹⁸ studied this transformation sequence using a differential thermal calorimeter and suggested that the exothermic reaction might be due to the crystallisation of amorphous silica formed from the metakaolin lattice or due to the dissociation of metakaolin. The assignment of the

exothermic dta peak to the crystallisation of amorphous silica can also be obtained indirectly by studying the effect of pressure on the metakaolin to spinel transformation.

Pressure effect on the metakaolin→spinel transformation: It has been reported earlier^{15,16} that the transformation temperature of metakaolin to spinel can be lowered by the application of an external stress. The effect of pressure on the phase transformation temperature of a system can be quantitatively estimated by the Clausius-Clapeyron equation. The metakaolin→spinel transformation can be written as follows:



In differential form, the Clausius-Clapeyron equation is,

$$\frac{dT}{dP} = \frac{T \Delta V}{\Delta H} \quad \dots (8)$$

If it can be assumed that the change of molar volume (ΔV) and the change of enthalpy (ΔH) are independent of pressure, then equation (8) can be integrated to,

$$\ln T/T_0 = \frac{\Delta V_0}{\Delta H_0} (P - P_0)$$

For a positive increment in pressure ($P - P_0 > 0$), it is apparent that if ΔV_0 and ΔH_0 have the same sign, $T > T_0$ and, if they are of opposite sign, $T < T_0$.

In the case of the metakaolin to spinel transformation, the ΔH has been reported¹⁷ to be in the range of -5 to -15.5 kcal/mole (ΔH is negative). The latest work by P. S. Nicholson and R. M. Fulrath¹⁸ suggests that for well crystallised and pure kaolinite, the ΔH is ~ -9 kcal/mole. The molar volume change (ΔV) for the transformation of metakaolin to spinel has been calculated using the data of G. W. Brindley and M. Nakahira¹, F. Freund¹⁹, and K. Range *et al*²⁰ and reported previously to be

$-79.13 \text{ cm}^3/\text{gm atom}^{16}$. Since $P - P_0$ is positive and both ΔV and ΔH are negative, application of an external pressure ($P - P_0 > 0$) should increase the transformation temperature, *ie*, T should be greater than T_0 , which is exactly opposite to that experimentally observed, where spinel was formed at a lower temperature under pressure ($T < T_0$). This contradiction can be resolved if it is considered that ΔH for the reaction metakaolin→spinel is positive (as ΔV is definitely negative). Furthermore, this reaction may be very sluggish and occurs over a range of temperature rather than at one temperature, as manifested in the transformation plasticity. The exothermic reaction in a dta plot ($\Delta H = -9$ kcal/mole) may be due to crystallisation of silica. If the existence of an amorphous phase is the primary reason for fluidity in this system (resulting in enhanced compaction), it is expected that the disappearance of this phase due to crystallisation will reduce or eliminate this plastic property (Fig 1). Compaction was stopped at the exothermic reaction temperature.

Summary

The phenomenon of transformation plasticity was investigated by studying the compaction behaviour of illite and kaolinite under isothermal conditions and at a constant heating rate. Transformation plasticity was encountered during the phase transition sequences of both illite to mullite and kaolinite to mullite. The compaction data were correlated with the dta plots of the same minerals. It was observed that although reasonable plasticity existed during the dehydroxylation reaction of kaolinite, very minimal plasticity was encountered with illite during the same reaction. In both cases, kaolinite and illite, enhanced compaction (*ie*, transformation plasticity) preceded the exothermic reaction in kaolinite (990°) and endothermic-exothermic reaction in illite (900° - 950°). It is proposed that the transformation of metakaolin to spinel and metakillite to mullite occurs before the reaction temperatures usually encountered

in dta plots of these minerals. The enhanced plasticity encountered in these systems are directly associated with these transformations and the exothermic peak in a dta plot is the result of crystallisation of amorphous silica, originally suggested by Nicholson and Fulrath.

Acknowledgment

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(Ms received September 4, 1975)

A HISTORY OF A RESEARCH PROJECT: GLASS-CERAMICS

G. P. SMITH*

Introduction

It is an axiom that major technological companies continue to exist because of the existence within them of an effective research and development organisation. It should be instructive in trying to determine how to maintain the effectiveness of such an organisation to examine the history of inventions and development in a successful project—in this case that of glass-ceramic materials in the laboratories of Corning Glass Works.

One of the less exact determinations which an historian must make is that of when his history is to begin. This is perhaps especially true of a history of technology, in which development depends on invention and also, in many instances, and just as truly, the specific invention is made as the result of earlier development. An inventor must be highly knowledgeable; it is rare and difficult for a neophyte to make a significant invention.

It is equally an axiom that an organisation exists, and progresses, because of the individuals who comprise it. Their skills, and their interests determine the course, and fate, of the organisation. So, in writing about a programme, it is necessary to write of the people who made it possible.

Pyroceram

Glass-ceramics, materials crystallised from glasses and now designated as *Pyroceram* materials, were formally announced in 1957. They introduced a revolutionary new concept in the field of inorganic non-metallic materials, changing an entire industry's practices in

forming and applying them. This is not to assert that crystallisation in glass was a new phenomenon—for thousands of years glassmakers had tried to prevent it in their glasses, and a continuing research at Corning and many other glass laboratories had been on formation of stable glasses which would not uncontrollably devitrify. Another continuing research of interest carried out at Corning was on why glasses colour as the result of interaction with radiation, and this is also pertinent to the history of the glass-ceramics.

Colour of glasses

Fully twenty years earlier, Dr R. H. Dalton had been conducting an investigation of methods of producing controlled colour patterns in glass. The phenomenon of solarisation of glass, of a change in its colour after exposure to sunlight, was well-known—old bottles in deserts and old window panes which have changed to purple after a long time in intense sunlight are familiar examples. It was also known that the colour of copper ruby glass results from the colloidal copper it contains, precipitated from the homogeneous glass melt either during initial cooling, or by reheating and then cooling the article made from the glass.

Behaviour of copper and gold ruby glass

Dalton found that a copper-containing glass exposed to ultraviolet light produced on subsequent heating and cooling, a more intense red colour than in unexposed glass. In 1940, Dr S. D. Stookey continued the study which Dalton had initiated of the behaviour of the copper ruby glasses. He determined that the ultraviolet radiation was absorbed by the copper ions, which

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were photochemically and thermally reduced to colloidal copper. Beautiful gold ruby glasses are highly prized for their clear and unique colour. To make a photosensitive gold ruby glass it is necessary to add small amounts of cerium as a photosensitiser to a gold-containing glass, since the gold ions do not themselves absorb the ultraviolet light. It is absorbed by the Ce^{3+} with emission of photoelectrons; subsequent heating of the glass allows capture of these electrons by adjacent gold ions in the glass network, and colloidal size particles are formed of these gold atoms. If the glass is irradiated through a pattern, such as a photographic negative, the same pattern will be reproduced in the glass. Fig 1 is of a photograph reproduced in glass by this process. S. D. Stookey later found that in proper compositions, the colloidal metal particles may be used to nucleate another phase, which in one case can be lithium metasilicate, thus making a photosensitive opal glass. Crystalline lithium



Fig 1
Photograph produced in a photosensitive glass

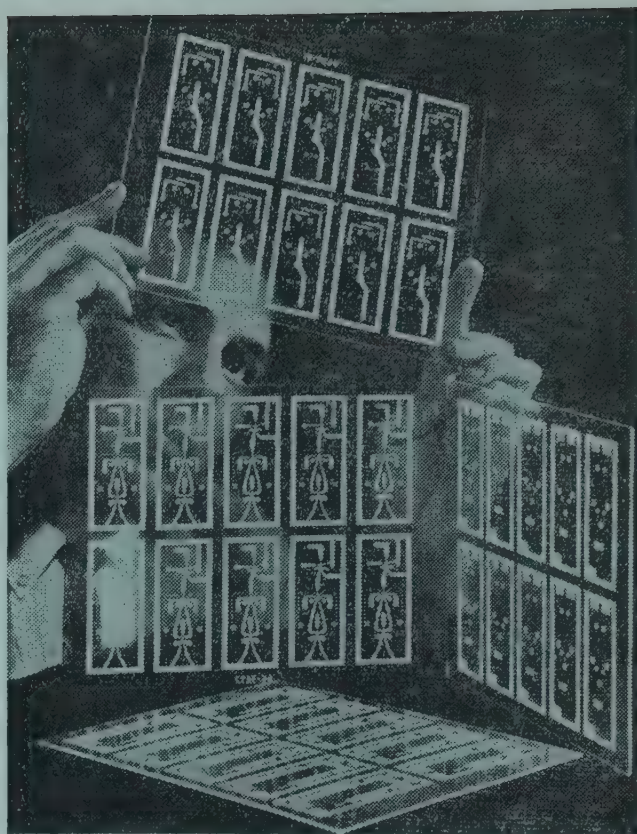


Fig 2
Fotoform parts produced by chemical machining of glass

metasilicate dissolves in hydrofluoric acid an order of magnitude or more faster than does the unexposed glass. This permits 'chemical machining' of glass, with production of intricately shaped *Fotoform* parts with dimensional tolerances comparable to those of the photographic process used in their production (Fig 2).

History of development of glass-ceramics

During this period of research on the phenomena of glass photosensitivity, various applications were found for articles made of these materials, and various product development, engineering, and production groups became involved. In the course of his continuing research in photosensitive glass, S. D. Stookey realised what profound changes could be brought about by a trace quantity of an effective nucleating agent. This realisation was brought into sharp focus by an accident, which as he relates turned out to be an important factor in the development

of glass-ceramics. In 1952, this accident was caused by the failure of a furnace temperature controller, which allowed the furnace to heat a plate of exposed photosensitive glass 300° hotter than the controlled setting. Expecting to find a pool of melted glass when he opened the furnace, he found instead, a plate of opaque, predominantly crystalline material that was much stronger and harder than the original glass. An invention is often the fortunate result of a seemingly unfortunate accident which happened to a very careful and observing observer. Serendipity forms a part of a good research programme.

This first ceramic from glass, a valuable material in itself, and one now used in several products, still required photonucleation. This was a cumbersome additional step in the process, and required protection of the glass against ultraviolet light before it was used. Continued compositional and processing research during this period permitted S. D. Stookey to conclude that controlled crystallisation involving thermal nucleation alone was both feasible and useful. The next stage, then, the development of thermally nucleated materials, involved the expansion of the knowledge gained in the photosensitive experiments described above to a general theory of nucleation, the search for other nucleating agents, and their use in a wide range of compositions.

When it became known how broad the range of thermally nucleated glass-ceramic compositions might be, the nature of the research was changed to a team effort, directed towards two goals. One objective was to explore the important composition fields, find the distinguishing general characteristics of the materials, classify them, and obtain the necessary information for preparing patent applications to protect this new area of glass research and processing. The other was to select a few promising compositions and begin the development of optimum processes for useful products. From this time onward, as compositions having new and desirable combinations of properties were developed, it became necessary to establish product development

groups. Other company divisions outside the laboratory began to take part, and the rapidly increasing number of problems became complex for all levels of management.

It is instructive now to look at the environment in which this group found itself: the industry, the company, the laboratory.

Production of glass items at Corning

The glass industry tends to distinguish itself from the ceramic industry in that its several fundamental processes, unlike its materials, are distinct. The processes are the basis of the classification of the industry into the flat glass, container glass, pressed and blown glass, and glass of specialty groups. In 1954, the sales volume in the United States were \$ 1822 million (flat glass: \$ 373, container glass: \$ 646, pressed and blown glass: \$ 416 and special glass: \$ 387 million respectively).

Corning Glass Works had sales of \$ 148 million in that year, with research and development costing \$ 4.5 million. Its manufacturing divisions reflected the kinds of markets which the company served: Electrical Products including light bulbs, radio bulbs, television bulbs, fluorescent tubing; Technical Products including laboratory glassware, chemical industry process ware, optical glass; Consumer Products including houseware, tableware, ovenware; and New Products including glass ultrasonic delay lines, glass resistors and glass capacitors.

The long-time and continuing company policy with respect to research is best indicated by the establishment of a glass laboratory at Corning in 1908, one of the first industrial laboratories in the nation.

Organisation and staffing pattern of the company

The laboratory during the mid-fifties was organised into departments like chemistry, physics, development, services—each with a manager reporting to the research director. In addition, a process research and development group formed with other research groups a

'melting research' group. This team played a vital and multiple role in bringing new developments into production. Part of the melting research group was housed in the research laboratory and its staff had traditionally worked closely with the research staff. Other parts of this group were housed in a pilot plant, and its staff had worked closely with manufacturing groups through process development and break-in stages. The research groups, in a laboratory surrounded by some of the manufacturing plants, were accustomed to close monitoring of melting and forming operations which were in transition from laboratory to production. That is, since the pilot plant concept had been of recent introduction, much experimental work was accomplished in the manufacturing plants, and research people took a personal interest in the progress of developing products; indeed, direct involvement was encouraged and expected.

Product history of the company

One important feature which helped determine the rapidity with which the technical and non-technical people grasped the significance of these new materials crystallised from glass was the company's product history. Since 1912, when W. C. Taylor and E. C. Sullivan had invented the low expansion borosilicate glasses to withstand heat shock, the first use of which was in lenses and lantern globes for railway signals, the company had recognised the great importance of a low thermal expansion for glasses. This awareness permeated the company. Some of the first glass-ceramics which contained lithia-alumina-silicates as the crystal phases had just this property, lower than most glasses, coupled with higher useful strength, so the advantages of commercial applications were immediately appreciated at all company levels.

Other compositions, in the magnesia-alumina-silicate composition area, had excellent dielectric properties at high frequencies, and were recognised as good candidates as transparent windows for high frequency signals. For a time,

therefore, compositional research, and the following development activities, followed these two main paths of low expansion coefficient and low microwave loss. The paths were different, and it is perhaps more instructive to follow that of the low expansion materials, recognising that the dielectric window materials and products were, and still are, produced by Corning.

Consumer products like dishes, pots and pans for cooking, baking, and serving foods, had been a continuing and stable business of Corning since shortly after the invention of the borosilicate glasses. Corning had developed a major business in transparent baking and cooking glassware. A parallel line was also based on opal glasses. The borosilicates had expansion coefficients only about one-third those of soda-lime-silicate glasses, and could be thermally strengthened for increased resistance to thermal shock. Even then they were not suitable for direct top-of-stove use. An alumino-silicate glass had been developed and manufactured for this purpose, but was only moderately successful.

It was immediately recognised that the low expansion glass-ceramics, in which an area of compositions was found which had the several other properties, *eg*, meltability, formability, colour, hardness, chemical durability, refractory character—suitable for this application, as well as an expansion coefficient much less than that of the borosilicates, would be highly attractive. There existed, at the time, no market in the sense of materials or products of similar properties. Competition was expected to be primarily from metallic containers; ceramic cookware never having been highly developed technically nor marketed aggressively. But the expected advantages of the new materials were so great not only for consumer but for technical applications that an intense development effort was mounted in 1957-58 leading to the melting of a lithia-alumina-silica glass in a full-scale production tank and its formation into sheet, rod, and tubing forms, as well as pressed and blown articles which were the precursors of the new *Pyroceram* cookware.

Technology of production

- The glass tank for the first product run was specially rebuilt for the 100° higher melting temperature and expected refractory corrosiveness of the new glass.
- The first metal moulds used to press this corrosive glass were worn out in just eight hours, compared to months or years expected in normal use.
- The dishes metal-marked severely. Micro-crystals at the surface abraded the edge of a knife drawn across it, leaving a stripe of metal that was not normally washed off.
- The surfaces showed a maze of very small cracks, resulting from differences in crystallisation of the glass at the surface and in the interior.

These and other problems were solved by composition and process changes, but were interesting while they lasted. That they were solved as rapidly as they were, or perhaps at all, was the result of an earlier decision of laboratory management to expand the research groups and not to yield to the temptation to concentrate manpower resources entirely on product development for immediate marketing. However, as interest in consumer products developed, services supporting research and development were brought in by, among others:

- The melting research melt shop to make more and faster experimental melts.
- The technical services group to measure chemical, physical, electrical properties.
- The product development group to evaluate proposed compositions and applications.
- The consumer marketing groups for shape, design, decoration, service tests and market evaluation.

Development of a glass-ceramics heat-exchanger

During this same time, one of the development groups in the laboratory had an unrelated project—a glass heat exchanger for a vehicular gas turbine engine (Fig 3). This exchanger, com-

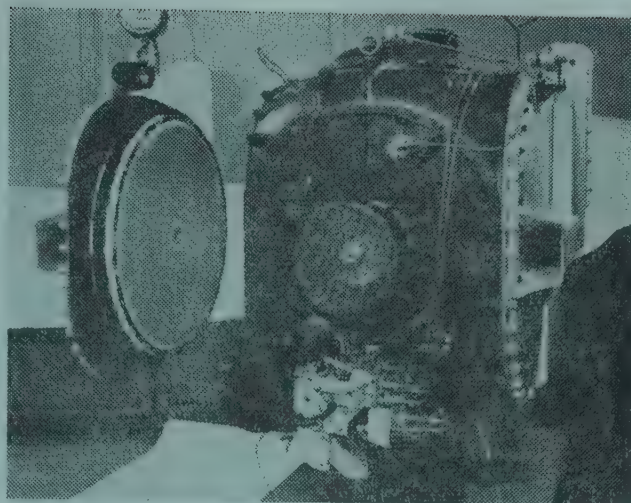


Fig 3
Glass-ceramic heat exchanger for gas turbine engine

monly in the form of a disc with many parallel axial passages, rotates continuously past intake and exhaust ports of the engine. One region of the exchanger is heated by the exhaust combustion products; the remainder preheats the incoming air. For an automobile engine, the energy exchanged is of the order of 200 million calories per hour. The original concept was of an array of thin-walled glass tubes—about 100,000 for a typical engine. With the advent of the low-expansion glass-ceramics, an entirely new manufacturing process for such a structure was developed, and for it a composition that had an effective zero expansion over the working temperature range of the heat exchanger, say 800° to room temperature.

Management problem

A very difficult management problem was to decide when and how to make public the new developments. An invention of such complexity and broad scope would require many years to perfect, so that immediate public announcement would be premature, but even then incomplete and distorted reports were beginning to circulate widely. Corning at that time was building new laboratory buildings. The announcement was made at the time of the dedication of these new Corning laboratories. The

response to this announcement was greater than almost anyone at Corning would have anticipated. About 10,000 requests for information or for samples resulted with most of these requests suggesting largely technical applications. In order to respond successfully to these and to tie together the activities of the various divisions of the company in this field, a coordinator for glass-ceramic materials was appointed. But it may be instructive that out of all these requests, and all these suggestions, none were found to be of any significant or lasting commercial interest. For several years, although they became large, the only applications of these glass-ceramic materials were in the consumer ware and microwave window areas.

Conclusion

To conclude, it is necessary to examine where Corning has come in the nearly two decades that have elapsed since the *Pyroceram* materials were announced. Corning itself has grown, from \$160 million sales in 1957 to \$1050 million in 1974. The laboratories were also outgrown in a decade, and we have again moved into a new complex of buildings of more than twice the floor space. The total complement of the Technical Staffs Division is now more than 800 people. A substantial portion of this growth, both research, development, and engineering and of the resultant sales of the company, is the result of the glass-ceramic invention. To iterate:

- Electromagnetic windows (radomes) based on cordierite, have been a continuing product, with very rigidly defined composition, property, performance and dimensional limits.
- New shapes, sizes, designs, have been developed so that there is now a large consumer product line of *Pyroceram* cooking and baking ware (Fig 4); the low expansivity is gained from precipitation of beta-spodumene or solid solutions of beta-spodumene and silica. In addition to the several factories in the United States, there is now a factory in The Netherlands,

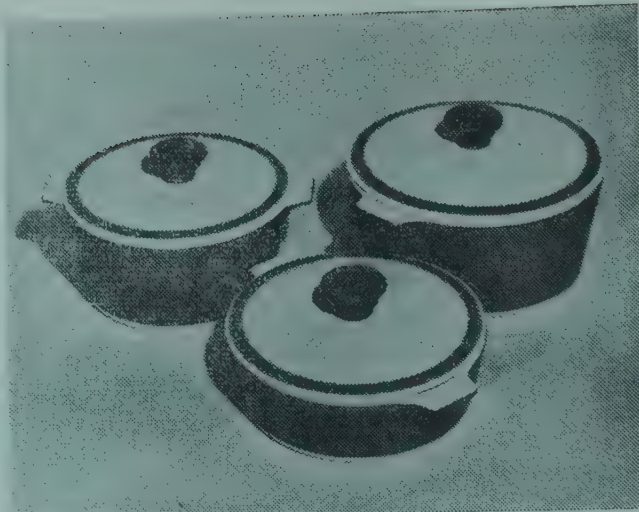


Fig 4
Cooking and bakingware from *Pyroceram*



Fig 5
Glass-ceramic articles produced by adding controlled electric heating elements

producing this ware, trademarked *Pyroflam*, for Europe. Controlled electric heating elements have been added to several of these glass-ceramic articles, such as

percolators, skillets, trays, and laboratory hot plates (Fig 5). When the crystals formed during their controlled precipitation are small enough so that they do not appreciably scatter light, the resultant glass-ceramic is transparent rather than opaque. Some very low expansivity materials are made in this way. The crystals are a beta-eucryptite silica solid solution.

- A lightweight dinnerware line was generated, with an opaque glass-ceramic core. The primary crystalline phase in this glass-ceramic is nepheline, a soda-alumina-silicate, deliberately chosen to produce a relatively high thermal expansion coefficient. It is in itself strong, but is made much stronger by a modified surface layer which has lower expansion, thereby putting the surface in compression (Fig 6).
- A method of forming and processing glass-ceramics in sheet form was developed. These materials, also based on beta-spodumene, are used as counter and laboratory bench tops (Fig 7). By adding controlled heating elements to the glass-ceramic in sheet form, an entirely new concept, *the counter that cooks* electric cooktop, was evolved (Fig 8).

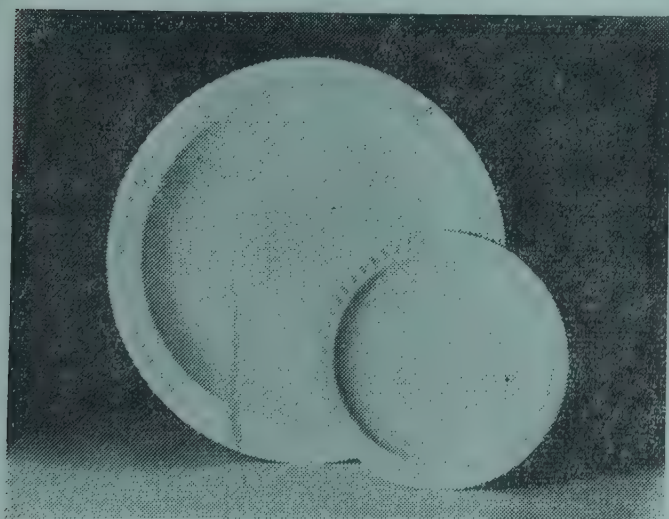


Fig 6

Light-weight dinnerware of glass-ceramics

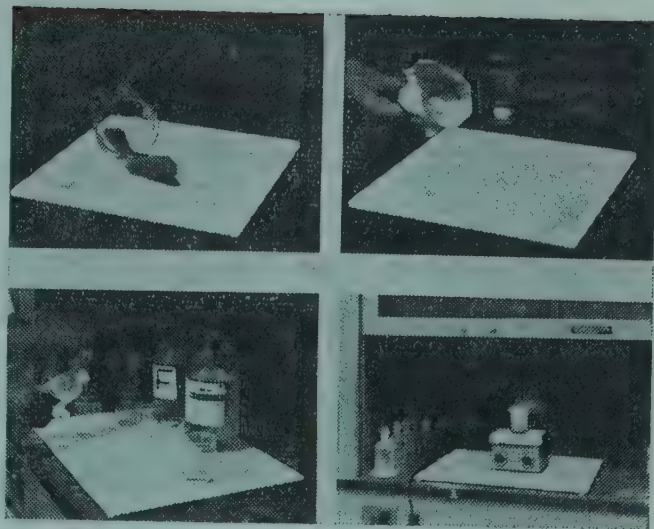


Fig 7

Beta spodumene glass-ceramics produced in sheet form used for counter and laboratory bench tops

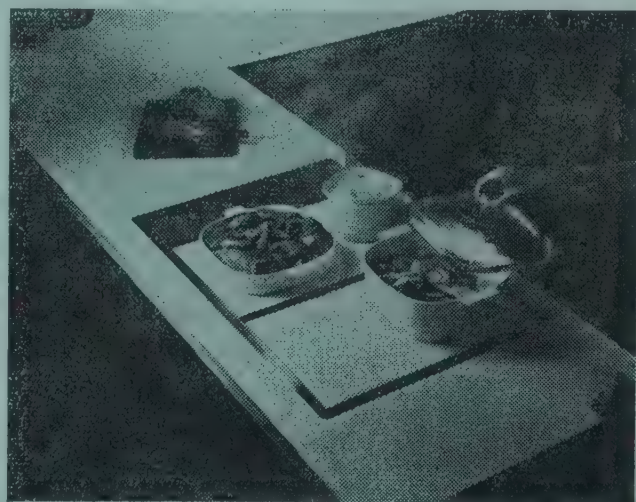


Fig 8

The counter that cooks electric cooktop

- High dielectric constant, therefore, miniature capacitors are now produced. From the proper glass composition, various ferroelectric crystals, such as titanates, or, for better electrical stability, mixed metal niobates, are precipitated. The dielectric constant may range from 300 to at least 1500, depending on crystal composition, concentration, and structure.
- It was found possible to make glass-ceramics which are machinable in the

metal-working sense, that is, machinable to precision tolerances with conventional metal-working equipment and tools (Fig 9). These materials, containing high percentages of crystalline phlogopite solid solutions, have also very good dielectric properties.

The course of development of the *Cercor* heat exchanger structure has been a long and often disappointing one. Vehicles—automobiles, trucks, off-the-road tractors with gas turbine engines are not yet in commercial production. But the promise still exists that they will

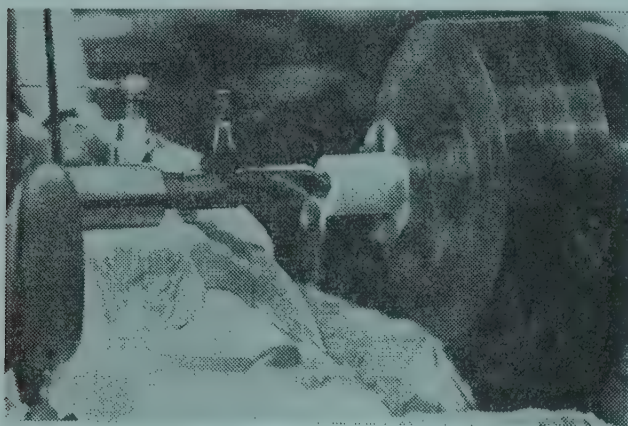


Fig 9
Machinable glass-ceramics with good dielectric properties



Fig 10
Photochromic glass used as lenses for prescription spectacles and sun glasses

be, and that their use will grow markedly. Some other alternatives, such as the Stirling engine, to the conventional internal combustion engine, have also received renewed attention, as has the recovery of heat from industrial processes, including incineration of waste materials. On the premise that gas turbine or Stirling engines must have a heat exchanger, that it must be ceramic rather than metal, and that Corning has a unique material and process technology for making it, we continue to interact closely with engine designers so that an usable, durable, efficient heat exchanger will be available when they need it.

Although it is not compositionally within the definition of glass-ceramics, this history could not be concluded without mention of an invention which would not have been possible without the knowledge of crystallisation kinetics in glasses gained by S. D. Stookey in his continuing work on these materials, and methods of process and control evolved by development, engineering and production groups for them. It is photochromic glass, in which the crystallised phase is a small amount of silver halide, which reacts reversibly to light. Now in production both in the United States and Europe as lenses for prescription spectacles and sun glasses (Fig 10), we expect that the use of these stable materials will be extended in many technical and industrial applications for the monitoring, control, or use of light.

This history should illuminate some of the more important aspects of Corning which have permitted it to be written:

- An early and continuing commitment of the company to the thesis that research is the basis for commercial progress.
- Integration of the programme and goals of the laboratory with those of the company.
- An awareness that research and development must be not only in materials, but in processes for their utilisation. The glass-ceramics are a combination of a

material and a process—they are equally important, and interdependent.

- A belief, in the laboratory and in the company, in freedom for, and encouragement of, growth of individuals in professional competence.
- A flexibility of organisation permitting the establishment of teams of experts, wherever in the company they are located, to meet specific objectives. The fixed policy is one of fitting the structure to the skills of the people available, rather than of fitting the people available to the structure. Equally important is the prompt dissolution of these teams once the objective is met, so that the expertise of its members can be best utilised on other projects.
- Establishment and maintenance of good

cooperation and of good communication in both directions between staff and operating groups. Research, development, engineering, production, sales, and general management all interact; the divisions between them are not as distinct as their names on organisation charts would indicate.

Acknowledgment

It is not possible for me to separately and properly acknowledge the work, published and private, of all my colleagues at Corning from which these illustrations have been drawn. But maintaining this climate for research in these laboratories should ensure that their new inventions, or new applications of existing ones, can only result in additional useful future products.

(Ms received September 4, 1975)

ABSORPTION CHARACTERISTICS OF Nd^{3+} ION IN GLASSES

A. SINGH AND P. NATH*

Introduction

K. Rosenhauer and F. Weidert¹ introduced spectrally pure neodymium oxide in silicate glasses and studied its absorption spectra. The smaller the ionic radius of the alkali or alkaline earth ion the more diffuse was the absorption band. In comparison to alkali ions the alkaline earth ions exerted a smaller perturbing influence. C. Hirayama and D. W. Lewis² observed similar results. The principal difference

between the earlier data and that found by C. Hirayama was in the increased resolution of the spectra which showed more of the fine structure. The potassium germanate and rubidium germanate had spectra identical with the corresponding potassium silicate glass. The spectra of Nd^{3+} ion in magnesium metaphosphate and alkali-borate glasses also had absorption bands in the same region as silicate. The extinction coefficient due to Nd^{3+} at 575 $m\mu$ peak increased in the order $\text{Li} < \text{Na} < \text{K} < \text{Ti}$, whereas, at 588 $m\mu$ it was in the order $\text{K} < \text{Li} < \text{Na} < \text{Ti}$.

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K. Hauptmanova *et al*³ observed that the absorption coefficient (K max) for $^4G_{9/2}$ (520 m μ) and $^4F_{7/2}$ (750 m μ) bands increased with decreasing ionic radii of alkali and alkaline earth ions. By comparing the results on R_2O , SiO_2 and $R_2O \cdot Al_2O_3 \cdot SiO_2$ it was concluded that the addition of alumina in glass did not affect the absorption spectra of neodymium ion⁴. Replacement of alkali by alkaline earth reduced the fine structure. With increasing Na_2O content from 8 to 25 mole per cent in $Na_2O-B_2O_3$ system the fine structure of the absorption spectra was reduced⁵. The molar extinction coefficient of Nd^{3+} in sodium borate glass containing 30 mole per cent Na_2O was 5 cm²/mole at 585 m μ .

The absorption spectra of Nd^{3+} ion in calcium lithium borate⁶ and La-Sr-Th- B_2O_3 ⁷ were similar to those obtained in binary borate glasses. On replacing B_2O_3 with SiO_2 or Al_2O_3 , the fine structure increased⁸. In magnesium-strontium phosphate glasses the spectra was intermediate between those for potassium silicate and lithium silicate glasses⁹.

F. H. Kang *et al*¹⁰, observed 12 absorption peaks between 300 and 2500 m μ in sodium silicate glass and assigned the energy levels.

In the present work the absorption characteristics of Nd^{3+} ion in ternary alkali-alkaline earth alumino-borate and aluminate glasses have been studied.

Experimental

Pure chemicals of 'Analar' grade were used for the preparation of glasses. Alkali and alkaline earth oxides were introduced as their respective carbonates, B_2O_3 as boric acid and Al_2O_3 as $Al(OH)_3$. Acid washed quartz was used for introducing SiO_2 . Neodymium was added as its oxide. Batch materials to yield about 100 gm of glass were weighed and mixed thoroughly. The glasses were melted in a Pt-2 per cent Rh crucible kept in an electric furnace for about 10 hours with intermediate crushing and remelting. After melting, the glasses were cast in a rectangular mould, annealed, ground

and polished. A protective coating was applied on the polished surfaces and the samples were kept in a desiccator. This coating was removed just before taking the absorption measurement on a recording Carry-14 spectrophotometer. The glasses were analysed for neodymium content following the sodium alizarin sulphonate method.

Results and discussion

The peak positions observed in glasses and in $LaCl_3$ crystal^{11,12} are approximately at the same wavelengths. The energy levels for the observed peaks in glasses were assigned after comparing the corresponding peaks in $LaCl_3$ crystal and are shown in Table I.

K. Hauptmanova *et al*³, assigned the levels for the peaks observed between 400 and 900 m μ range in alkali-alkaline earth silicate glasses. The peaks at 744 and 740 m μ wavelengths were designated by these authors as $^4S_{3/2}$ and $^4F_{7/2}$ respectively, whereas, E. H. Carlson¹¹ and G. H. Dieke *et al*¹² have reported these peaks as $^4F_{7/2}$ and $^2S_{3/2}$ respectively. K. Hauptmanova observed two peaks at 585 and 575 m μ wavelengths and assigned them as $^2G_{7/2}$. In $LaCl_3$ crystals, these peaks have been designated as $^4G_{5/2}$ and $^2G_{7/2}$ respectively. In the present series of glasses both these peaks have been observed and levels have been assigned as in $LaCl_3$ crystal. K. Hauptmanova assigned $^4G_{9/2}$ level for the peak at 513 m μ , whereas, E. H. Carlson¹¹ and G. H. Dieke¹² considered it as $^2G_{9/2}$. The peak at 472 m μ which was due to $^2D_{3/2}$ level and found in lithium alumino-borate glass has not been reported earlier in glass. Below 400 m μ , K. Hauptmanova *et al*³, did not assign the levels which have been designated in the present work and shown in Table I.

It is observed (Table I) that with increasing ionic radius of the alkali ion in the glasses, some of the absorption peaks shifted towards the shorter wavelengths. In alkaline earth alumino-borates the reverse was observed and some of the peaks shifted more towards the longer wavelengths with increasing ionic radius

of the alkaline earth ion. When alkali ions were replaced by alkaline earth ions, the peak positions shifted slightly towards the longer wavelengths. The absorption peaks of Nd^{3+} ion in aluminate glass were at longer wavelength than those in alkali and alkaline earth aluminoborate glasses.

The effect of alkali ions on the absorption spectra of neodymium ion in ternary aluminoborate glasses is shown in Figs 1 and 4. The molar extinction coefficients ($E_{\text{Nd}^{3+}}$) at the absorption peaks were calculated from the optical density and other data, and are summarised in Table II. $E_{\text{Nd}^{3+}}$ at all the absorption

TABLE I

Assignment of the peaks observed in neodymium containing glasses, ground level: $^4\text{I}_{9/2}$

Energy level	Nd ³⁺ ion in LaCl ₃ crystal	Observed peak positions in ternary aluminoborates (in mμ)						Aluminate	Sodium silicate (after Kang ¹⁰)
		Li	Na	K	Ba	Sr	Pb		
1	2	3	4	5	6	7	8	9	10
$^4\text{I}_{13/2}$	2495								2500
$^4\text{I}_{15/2}$	1665								1630
$^4\text{F}_{3/2}$	874	870	870	870	877	877	877	885	885
$^4\text{F}_{5/2}$	801	805	800	795	810	805	808	812	813
$^4\text{F}_{7/2}$	744	744	744	744	750	745	748	755	744
$^2\text{S}_{3/2}$	739	740	740	740	740	740	740	745	—
$^4\text{F}_{9/2}$	679	680	680	675	685	680	680	690	692
$^2\text{H}_{11/2}$	627	630	625	625	627	625	625	625+	—
$^4\text{G}_{5/2}$	585	588	585	585	588	585	585	595	588
$^2\text{G}_{7/2}$	579	575+	575+	575+	575+	575+	575	585	575
$^4\text{G}_{7/2}$	525	530	525	525	530	527	525	530	537*
$^2\text{G}_{9/2}$	513	515	512	512	515	512	512	518	517
$^4\text{G}_{9/2}$	475	478	475	475	475	475	475	475	—
$^2\text{D}_{3/2}$	472	474							
$^4\text{G}_{11/2}$	465	465	460	460	465	465	465		
$^2\text{P}_{1/2}$	431	435	430	430	435	432	430	433	433
$^2\text{D}_{5/2}$	420	418	418	418	418	418			
$^2\text{P}_{3/2}$	384								
$^4\text{D}_{3/2}$	357	360	360	360	360	355	365	358	
$^4\text{D}_{5/2}$	356								
$^2\text{I}_{11/2}$	354	355	350	348	352			352	350×
$^4\text{D}_{1/2}$	351								

+Shoulder; ×_D; *²K_{13/2}

peaks except at $585\text{ m}\mu$ ($^4I_{9/2} \rightarrow ^4G_{5/2}$ transition) increases with increasing ionic radius of the alkali ion. At $585\text{ m}\mu$ peak molar extinction coefficient increased on replacing Li by Na ion but decreased when Na was replaced by K.

The effect of mutual replacement of bivalent cations is shown in Fig 2 and Table III. Extinction coefficient decreased with increasing ionic

radius of the alkaline earth ion at all peaks except at $585\text{ m}\mu$ ($^4I_{9/2} \rightarrow ^4G_{5/2}$ transition) at which it increased. In lead glasses the absorption intensity was more than that in glasses containing strontium or barium.

The absorption spectra of Nd^{3+} in aluminate glass (Al_2O_3 38.0, SiO_2 7.0, CaO 47.0, MgO 3.5, Na_2O 3.5, Li_2O 1.0 wt per cent) are shown

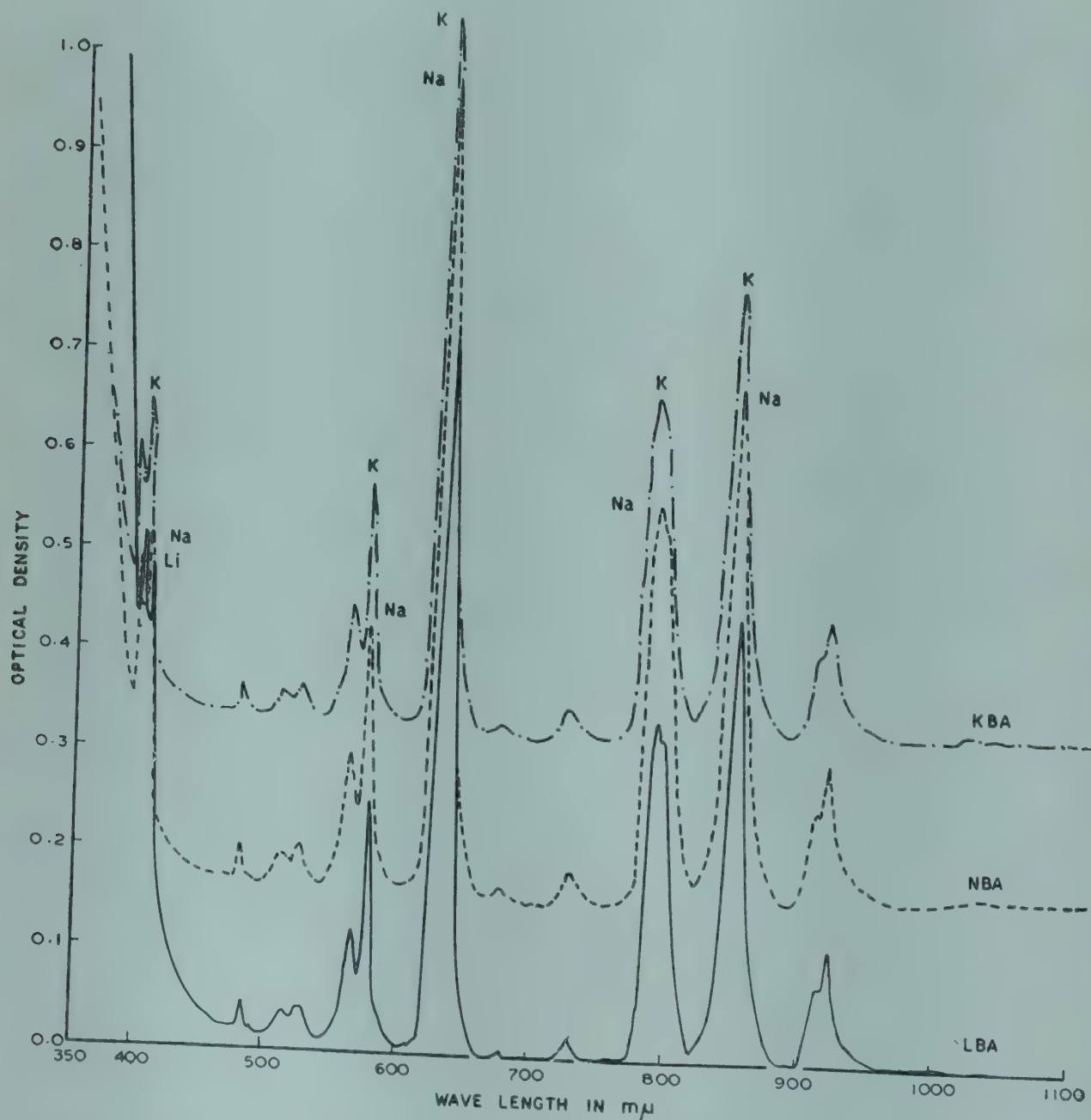


Fig 1

Absorption spectra of neodymium ions in alkali-alumino-borate glasses. The zero of the absorption curves for sodium and potassium glasses have been shifted upwards by 0.2 and 0.3 OD respectively

in Fig 3 and compared with those of sodium aluminoborate glass. The molar extinction coefficients ($E_{\text{Nd}^{3+}}$) of these glasses are given in Table III. In aluminate glass $E_{\text{Nd}^{3+}}$ at all the peaks except at $598 \text{ m}\mu$ ($^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$ transition) were greater than those in sodium aluminoborate glass, whereas, it was reverse at $598 \text{ m}\mu$.

In all the above three types of glasses, anomaly in extinction coefficient for $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$ transition occurred. Similar anomaly for this transition was found by C. Hirayama *et al*² in alkali silicate glasses. It is not possible at this stage to explain this discrepancy. †

The shape of the absorption spectra in alkali-

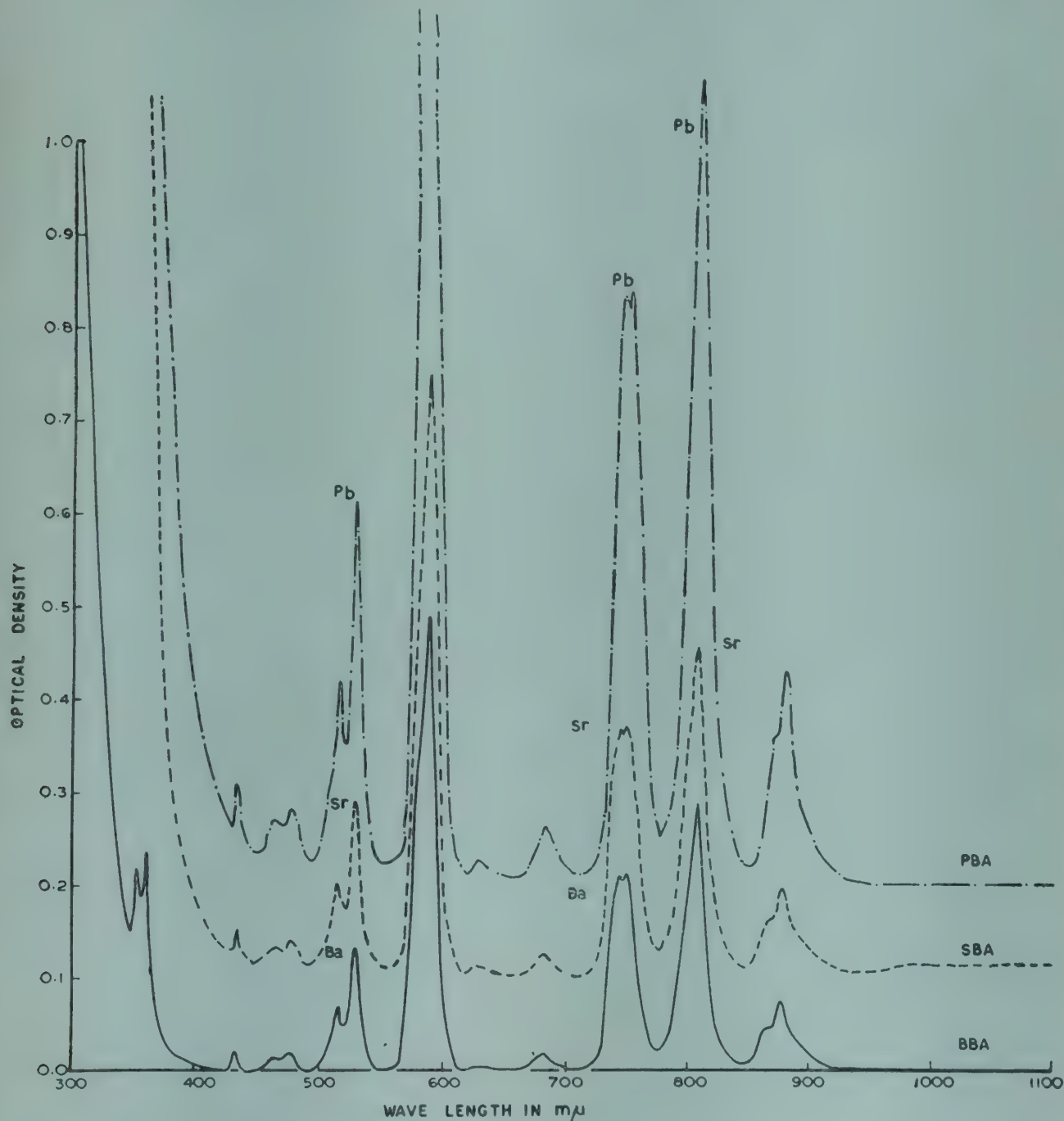


Fig 2

Effect of divalent cations on the absorption spectra of neodymium ions in ternary aluminoborate glasses. The zero of the absorption curves for strontium and lead containing glasses have been shifted upwards by 0.1 and 0.2 OD respectively

TABLE II

Effect of alkali ions on the absorption spectra of neodymium ion in aluminoborate glasses. Glass composition: R_2O 15, Al_2O_3 10, B_2O_3 75 mole per cent and Nd_2O_3 2 wt per cent

Energy level	Approximate wavelength (m μ)	Lithia glass t=4.03 mm		Soda glass t=4.4 mm		Potash glass t=4.174 mm	
		OD	E _{Nd}	OD	E _{Nd}	OD	E _{Nd}
$^4F_{3/2}$	870	0.112	0.613	0.148	0.843	0.190	1.217
$^4F_{5/2}$	805	0.441	3.296	0.520	3.608	0.515	3.739
$^2S_{3/2}$	740	0.337	2.448	0.402	2.731	0.410	2.924
$^4F_{9/2}$	680	0.022	—	0.038	0.012	0.098	0.503
$^4G_{5/2}$	585	0.715	5.530	0.825	5.875	0.788	5.858
$^4G_{7/2}$	530	0.252	1.755	0.292	1.935	0.325	2.264
$^2G_{9/2}$	515	0.125	0.719	0.150	0.857	0.198	1.279
$^2P_{1/2}$	435	0.048	0.091	0.058	0.173	0.118	0.658
$^4D_{3/2}$	360	0.482	3.630	0.390	2.641	0.402	2.862
$^4D_{1/2}$	355	0.518	3.924	0.342	2.506	0.358	2.521
$^2I_{11/2}$	330	cut off		cut off		cut off	

TABLE III

Effect of alkaline earth ions on the absorption spectra of neodymium ion in alkaline earth aluminoborate and aluminate glasses. Glass composition: RO 30, Al_2O_3 10, B_2O_3 75 mole per cent and Nd_2O_3 2 wt per cent

Energy level	Approximate wavelength (m μ)	Barium glass Nd_2O_3 2 wt per cent, t=2.201 mm		Strontium glass Nd_2O_3 2 wt per cent, t=2.29 mm		Lead glass Nd_2O_3 2 wt per cent, t=2.614 mm		Aluminate glass Nd_2O_3 4 wt per cent, t=2.22 mm	
		OD	E _{Nd}	OD	E _{Nd}	OD		OD	E _{Nd}
$^4F_{2/3}$	877	0.075	0.318	0.100	0.641	0.332		0.365	1.615
$^4F_{5/2}$	810	0.288	2.650	0.365	3.640	0.975		0.648	3.082
$^4F_{7/2}$	750	0.215	1.851	0.275	2.621	0.745		0.535	2.496
$^2S_{3/2}$	740	0.210	1.796	0.272	2.587	0.738		0.540	2.522
$^4G_{5/2}$	588	0.490	4.862	0.652	6.888	0.130		1.000	4.906
$^4G_{7/2}$	530	0.135	0.974	0.195	1.716	>1.0		0.762	3.672
$^2G_{9/2}$	515	0.072	0.285	0.108	0.731	0.515		0.732	3.517
$^2P_{1/2}$	435	0.025	0.230	0.055	0.131	0.322		0.810	3.921
$^4D_{3/2}$	360	0.238	2.102	cut off		0.210		1.480	7.393
$^2I_{11/2}$	352	0.220	1.905			cut off		1.465	7.316
$^4D_{1/2}$	305	cut off							cut off at 322

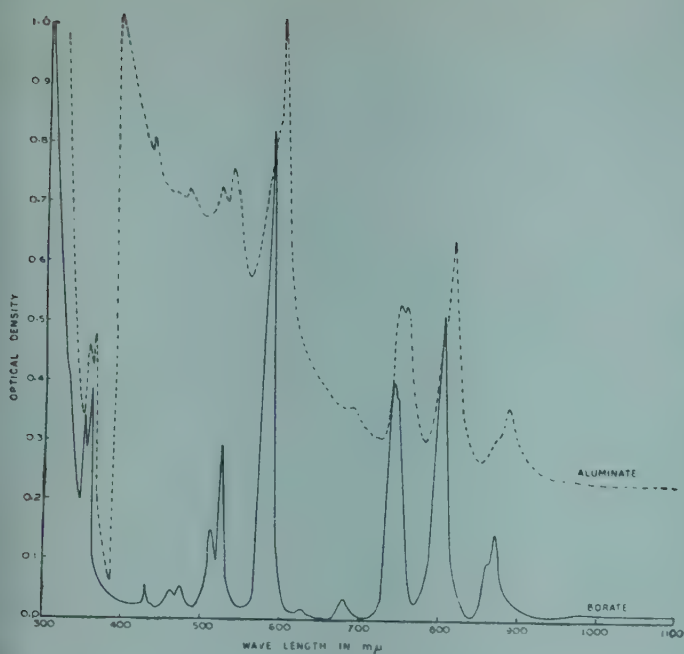


Fig 3

Absorption spectra of neodymium ions in aluminate glass as compared to that in sodium-alumino-borate glass

alumino-borate glasses containing lithium, sodium and potassium were similar. C. Hirayama⁵ had observed similar behaviour in binary alkali borate glasses. In alkali-alumino-borate glasses only shoulder was observed for $^4F_{7/2}$ level but in alkaline earth borate glasses distinct peak was found.

Absorption spectra of rare earths arise due to internal transition inside the 4f shell. As these are forbidden transitions, the molar extinction coefficients are expected to be very low. C. Hirayama^{2,5} had determined the extinction coefficient at 575 and 585 mμ peaks in alkali silicate and borate glasses and found to be between 3 and 7 cm²/mole. In the present series of glasses the extinction coefficients have been determined at all the absorption peaks and are given in Tables II and III. These results show that the absorption intensities are low and the low extinction coefficients show that the peaks

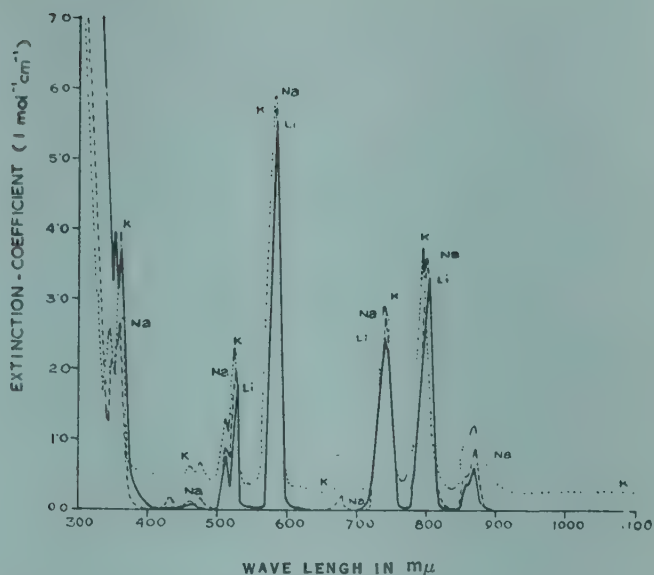


Fig 4

Extinction coefficient of Nd^{3+} in alkali-alumino-borate glasses as a function of wavelength

are due to forbidden transitions occurring in the 4f shell.

Summary

Absorption characteristics of Nd^{3+} ion in ternary alumino-borate glasses having the general composition: R_2O 15 / RO 30, Al_2O_3 10, B_2O_3 75 and aluminate glasses were studied in the range 300–1100 mμ wavelength and 17 absorption peaks were observed. Energy levels for these peaks were assigned. With increasing ionic radii of the alkali and alkaline earth ions, the molar extinction coefficient at various peaks in the visible range except at 585 mμ increased. At 585 mμ extinction coefficient increased in the order $Li < K < Na$ and $Ba < Sr$. The absorption peaks in aluminate glass are at longer wavelengths than those in alkali and alkaline earth alumino-borate glasses.

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INVESTIGATION ON SOME NEW SOURCES OF RAW MATERIALS FOR GLASS INDUSTRY : PART V — SILICA DEPOSIT FROM KALYASOTA-MAHESHNADI OF PURULIA DISTRICT, WEST BENGAL

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Introduction

Five samples of sandstone were received from the West Bengal Mineral Development and Trading Corporation, a Government of West Bengal Undertaking, to evaluate their suitability in glass manufacture.

Description of the deposit

All the five samples, marked T_1 , T_2 , T_3 , T_4 and KgD_5 , were derived from the deposit located in Kalyasota-Maheshnadi area of Purulia district, West Bengal. The area is located just at the tip of the eastern abutment of Panchet Dam. The sandstone bed is commercially workable. The deposit is wedge shaped gradually thickening from 18 metres at the

south to over 80 metres in the north within a strike length of 725 metres. Out of total reserve of 0.45 million ton, the estimate of washed sand is stated to be 0.25 to 0.30 million ton.

Physical and microscopic examination of the samples

Samples as received: The samples as received were of creamish yellow colour. Sample T_1 showed pale creamish yellow and T_3 was pinkish yellow. The samples consisted mostly of coarse to fine sand grains and were mixed with small friable lumps. On touching the sand, clayey matter stuck to the finger showing the presence of clay. All the samples consisted mainly of quartz and potash feldspars, often altered to kaolin. Quartz grains were mostly subrounded and feldspar grains were prismatic. Ferruginous

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material was present, associated with the grains. Sample T₃ contained some brownish black opaque mineral, probably of iron. The mineral composition of these samples suggested that they were felspathic sandstone.

Samples after sieving and washing: The samples after sieving and washing were found to consist mainly of quartz and a little of potash feldspar. They were almost free from ferruginous matter. Sample T₂ and T₃ contained a few quartz grains coated with clayey matter.

Mechanical analysis

Considerable portion of the sample was in the form of powder. The lumps present in the sample consisted of loosely held sand grains which could be easily powdered in porcelain mortar by gentle pressure. The sand grains thus obtained from the sample were subjected to sieve analysis. In commercial glass melting practice, the grains of sand coarser than 600 micron IS sieve (25 mesh BS sieve) and finer than 125 micron IS sieve (120 mesh BS sieve) are generally not used. On screening through these sieves, the useful portion of the sand was found to range from 50 to 65 per cent. The rejected fraction of 35 to 50 per cent were mostly finer grains (-125 micron IS). The proportion to be rejected would also depend on the commercial crushing method adopted.

Chemical analysis

Chemical analysis was done on the five re-

presentative samples of grain size $-600+125$ micron IS sieve before and after washing with water, drying and passing through a magnetic separator. The results of chemical analysis are shown in Tables I and II.

Sieved, unwashed and unmagnetted: It would be seen (Table I) from the results of chemical analysis that the five sieved samples ($-600+125$ IS) before washing and magnetting were very much deficient in their silica content. Silica ranged from 88.4 to 92.9 per cent, whereas, a minimum of 97 per cent is specified in the IS specification for Glass Making Sands (IS: 488-1963). Moreover, percentage of Al₂O₃ was too high ranging from 3.6 to 6.4 per cent. The low silica and high alumina contents indicated the presence of felspathic and clayey minerals.

Sieved, washed and magnetted: The sieved samples were further processed by water washing and magnetting. Complete chemical analysis (Table II) for all constituents was done on these processed samples.

A large amount of iron was removed on washing and magnetting the sieved fraction (Table II). Samples T₁, T₂, T₄ and KgD₅ could be beneficiated to have iron contents within the limit recommended for grade 2 sand of IS: 488-1963. The glasswares made from them, like bottles for beer, and aerated water, would be slightly tinted.

Regarding SiO₂ content of sample T₂, it will be seen that there was remarkable improvement on washing. SiO₂ content increased to 97.8 per

TABLE I

Chemical analysis (per cent) of sieved samples of sandstones from West Bengal*

Sample mark	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	LOI
T ₁	91.1	4.6	0.09	Tr	0.71	Tr	1.93	0.10	1.30
T ₂	92.9	3.6	0.12	Tr	0.43	Tr	1.54	0.09	1.12
T ₃	89.2	5.5	0.96	Tr	0.43	Nil	2.04	0.12	1.56
T ₄	89.5	5.7	0.26	Tr	0.43	Nil	2.17	0.13	1.47
KgD ₅	88.4	6.4	0.19	Tr	0.28	Tr	3.31	0.16	1.19

*between -600 and $+125$ micron IS sieve

TABLE II

Chemical analysis (per cent) of sieved, washed and magnetised samples

Sample Mark	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	LOI
T ₁	95.4	2.16	0.064	0.43	0.88	0.09	0.40
T ₂	97.8	0.91	0.048	0.18	0.58	0.07	0.34
T ₃	95.9	2.02	0.032	0.30	0.98	0.08	0.49
T ₄	96.3	1.72	0.048	0.24	1.02	0.09	0.35
KgD ₅	95.6	2.17	0.064	0.21	1.29	0.13	0.33

cent which is within the Indian Standard specification limit. This sample, therefore, on sieving, washing and magnetting, was beneficiated to grade 2 sand of IS: 488-1963 which is suitable for manufacture of slightly tinted glass ware.

With regard to the SiO₂ content of T₁, T₃, T₄ and KgD₅, it will be seen that the SiO₂ in each one of them was lower than 97 per cent which is the minimum specified in IS: 488-1963. One favourable point, however, is noticed that there was considerable increase in SiO₂ content and lowering of Al₂O₃ on processing. The SiO₂ content ranged between 95 and 96 per cent and Al₂O₃ between 1.7 and 2.2 per cent.

The sands had about 35 to 50 per cent of the grains finer than 125 micron which are not suitable for glass manufacture. Their suitability in ceramic industry was investigated. It was found that except sample T₃, the other four

sands were suitable for crockery manufacture. Sample T₃ may be used for stoneware type of crockery. All of them could be used for manufacture of insulators, sanitarywares and wall tiles. For use in the manufacture of these ceramic articles, the sands have to be ground to 6 to 5 mesh IS sieve.

Summary

Five samples of sandstone from Kalyasota-Maheshnadi area of Purulia district in West Bengal sent by West Bengal Mineral Development and Trading Corporation were evaluated for their suitability for glass making. Sample T₂ on sieving, washing and magnetting conformed to grade 2 of IS: 488-1963 and samples T₁, T₄ and KgD₅ on beneficiation did not conform to any grade of this standard because of low silica content although their iron contents are within the range of grade 2 of IS: 488-1963. The sandstones may be used in the manufacture of ceramic articles after grinding to 6 to 5 mesh IS sieve. As the deposit is reported to be extensive, further investigation may be needed to see if sufficient coarser material may be obtained which on secondary crushing might yield glass making sand at a reasonable cost.

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THERMAL EXPANSION BEHAVIOUR OF SOME SULPHATE CONTAINING LEAD GLASSES

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Introduction

Disposal of highly radioactive waste generated by the atomic industry, in the form of a glass is under consideration in a number of countries. The incorporation and retention of this waste in a glassy matrix poses several problems, especially if the waste solution contains sulphates. Incorporation of SO_4^{2-} in a sodium borosilicate glass¹ leads to phase separation and precipitation of Na_2SO_4 , due to the incompatibility of SO_4^{2-} and the borosilicate system. Na_2SO_4 is compatible with phosphate system² but the use of phosphate systems for waste disposal is undesirable because of severe corrosive effect on the process equipment and materials during the vitrification/solidification process. Further, the glass that is finally formed with the waste must have as low a leachability (high chemical durability) and thermal expansion as possible.

Various studies³ have shown that sulphate in the form of PbSO_4 is compatible with the silicate system. However, the effects of Na_2SO_4 and B_2O_3 in such system has not been well investigated.

As a part of our programme on waste immobilisation, we have, therefore, investigated lead silicate glasses for their ability to incorporate sulphates (Na_2SO_4) in presence and absence of B_2O_3 . Various parameters such as phase separation, chemical durability, refractive index, sulphate volatilisation, *etc.*, have been studied. In this communication, we report on the thermal expansion behaviour of these compositions which had formed a homogeneous glass.

Experimental

Glass composition: Two series of base glass com-

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positions with and without B_2O_3 were chosen. These are referred to as series I and series II (Table I) in all subsequent discussions.

In series I, there is progressive addition of Na_2O (Sl No 1-4); Na_2SO_4 (Sl No 5-8) and SO_3 (Sl No 9-12) with a corresponding decrease in the amount of the base glass; the base glass composition remaining constant. Thus this series has a general formula: $(100-x_1) S_1 + A$, where S_1 represents the mole fraction of the base glass of series I, x_1 is the mole per cent of the additive A which is varied as indicated in Table II.

In series II, there was a further subdivision, *ie.*, series IIA and IIB. In series IIA (Table III) the amount of SO_3 as PbSO_4 was kept constant and SiO_2 was partly replaced by B_2O_3 and PbO partly replaced by Na_2O . The general composition in this series could be represented as: $(41.26-x) \text{SiO}_2$, $(50-y) \text{PbO}$, 8.74SO_3 , XB_2O_3 , YNa_2O . In series IIB (Table IV) the amount of lead as PbO was kept constant and the amount of SO_3 was progressively decreased with a corresponding increase in SiO_2 content. These glasses corresponded to a general formula: $(41.26+x) \text{SiO}_2$, 50PbO , $(8.74-x) \text{SO}_3$.

Materials and method of glass preparation: Since this was meant to be fundamental investigation only analytical grade reagents were used.

TABLE I

Base glass composition (mole per cent) and thermal expansion

Sl No	SiO_2	B_2O_3	PbO	SO_3	$\alpha \times 10^6 \text{K}^{-1}$ (425-475K)
I	21.69	37.41	40.90	—	8.0
II	41.26	—	50.00	8.74	12.5

H₃BO₃, Na₂B₄O₇ · 10H₂O (source material for Na₂O in series I glasses), Na₂SO₄, PbSO₄, PbO, Na₂CO₃ (source material for Na₂O in series IIA glasses) were of analytical grade purity. Na₂SO₄, PbSO₄ and optical glass grade quartz were all ground to -100 mesh before use. Quartz powder was used as a source for SiO₂ while PbSO₄ formed the source for SO₃ in series I base glass. Additional lead due to PbSO₄ addition is compensated by removing the equivalent PbO from the base glass.

All glasses were prepared at fixed temperature of 1170K in platinum crucible on 50 gm scale. The mixtures were first melted for four hours and then poured on a stainless steel(ss) plate. The poured glass was crushed and remelted for additional two hours. A part of the melt was then poured into a ss mould of 1.5 cm internal diameter and 1.5 cm height and the remaining was poured over the ss plate. The mould was imme-

TABLE II

Composition (mole per cent) and thermal expansion of glasses of series I

Sl No	SiO ₂	B ₂ O ₃	PbO	Na ₂ O	Na ₂ SO ₄	SO ₃	$\alpha \times 10^6 \text{ K}^{-1}$ (425-475 K)
1	21.41	36.91	40.36	1.30	—	—	9.5
2	21.13	36.46	39.87	2.54	—	—	9.0
3	20.62	35.55	38.86	4.97	—	—	10.5
4	20.12	34.69	37.92	7.25	—	—	11.0
5	21.41	36.93	40.36	—	1.30	—	7.0
6	21.13	36.45	39.87	—	2.54	—	8.5
7	20.62	35.55	38.86	—	4.97	—	10.5
8	20.12	34.69	37.92	—	7.27	—	10.0
9	21.41	36.93	40.36	—	—	1.30	8.0
10	21.13	36.45	39.87	—	—	2.54	9.0
11	20.62	35.55	38.86	—	—	4.97	9.0
12	20.12	34.69	37.92	—	—	7.27	9.0

TABLE III

Composition (mole per cent) and thermal expansion of glasses of series IIA

Sl No	SiO ₂	SO ₃	PbO	Na ₂ O	B ₂ O ₃	$\alpha \times 10^6 \text{ K}^{-1}$ (425-475K)
1	41.26	8.74	48.84	1.16	—	13.0
2	41.26	8.74	47.68	2.32	—	14.0
3	41.26	8.74	45.46	4.54	—	—
4	41.26	8.74	43.38	6.62	—	—
5	36.70	8.74	50.00	—	4.56	11.0
6	32.13	8.74	50.00	—	9.13	11.0
7	27.57	8.74	50.00	—	13.69	10.5
8	23.01	8.74	50.00	—	18.25	11.0

diately put into an annealing furnace which had been heated to 660K. The furnace was immediately switched off after closing the door. After 16 hours the glass pellet was taken out from the annealing furnace. Out of the annealed pellet, pellet of exactly 1.25 cm dia × 1 cm height was made with the help of trepanning machine and subsequently fine grinding of the sides. The ends were polished flat. These pellets were used for dilatometric studies. The fraction of the melt poured over ss plate was collected after 15 minutes in a marked container to study the other product characteristics.

Equipment: Type LKB 3185 quartz dilatometer which could measure dilation of solids upto 1273K was utilised for thermal expansion measurements. The sample (1.25 cm diameter × 1 cm length) was kept between two small quartz discs which were placed inside the quartz tube. The entire assembly along with quartz extension rod and the thermocouple was inserted in the furnace which was thermally insulated. Calibrated chromel-alumel thermocouple was placed near the sample and was used for sample temperature measurement. The dilation of the sample was read on a calibrated 'Baty Dial Gauge' which could read the dilation

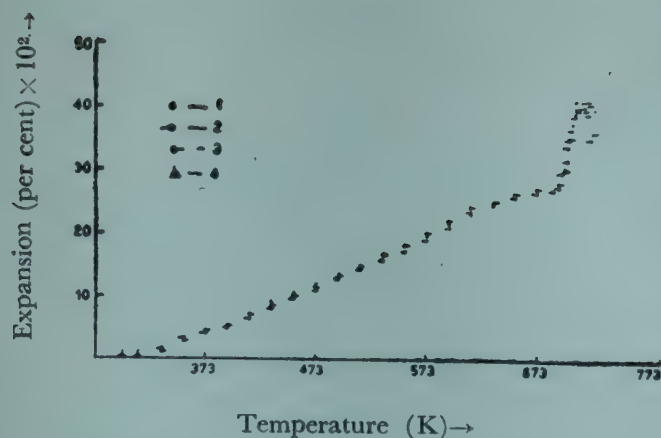


Fig 1

Reproducibility of expansion of series I base glass (per cent):
1-first pellet; 2-second pellet; 3-third pellet; 4-common
point to 1st, 2nd and 3rd pellet

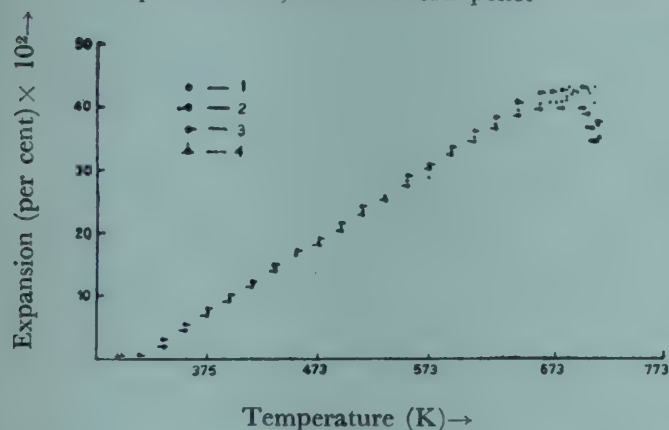


Fig 2

Reproducibility of expansion of series II base glass
(per cent) : 1-first pellet; 2-second pellet; 3-third pellet;
4-common point to 1st, 2nd and 3rd pellet

with an accuracy of ± 0.0005 mm. The rate of heating of the sample was controlled by means of variac. A heating rate of 2K/min was used throughout the investigations. The dilatometer was calibrated using pure high density nuclear ThO_2 pellet.

Results

Figs 1 and 2 show the per cent expansion as a function of temperature for series I and II base glass respectively. Three runs were made with three different pellets for each base glass. These values indicate the reproducibility of the measurement. Both the base glasses have nearly the same dilatometric softening temperature, *ie*, 716K for first and 713K for second.

It is to be noted that in the vicinity of the

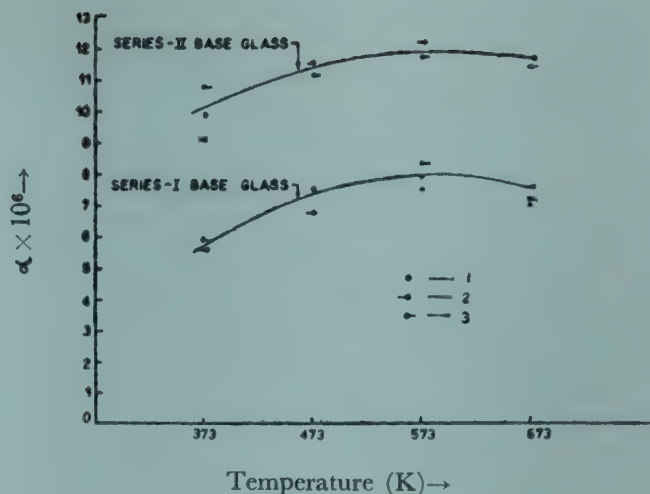


Fig 3

The variation of linear coefficient of expansion (α) with temperature for series I and II base glasses: 1-first pellet; 2-second pellet; 3-third pellet

TABLE IV

Composition (mole per cent) and thermal expansion of glasses of series IIB

Sl No	SiO_2	SO_3	PbO	$\alpha \times 10^6 \text{K}^{-1}$ (425-475K)
1	42.73	7.27	50.00	12.0
2	45.03	4.97	50.00	11.0
3	47.46	2.54	50.00	11.0
4	48.70	1.30	50.00	10.0

softening temperature, there is sharp rise in per cent expansion for series I base glass in contrast to series II base glass. This effect is attributed to the presence of B_2O_3 in series I base glass and absence of B_2O_3 in series II base glass. This influence of B_2O_3 on the expansion behaviour in the vicinity of the softening temperature is seen clearly in the glasses (Sl No 5-8) of series II base glass in which B_2O_3 is progressively substituted for SiO_2 . This observation is in accordance with the observation made by L. F. Oldfield⁴, "two borosilicate glasses may have identical expansion coefficients (20° - 350°) but have different expansion characteristics in their annealing ranges independently of heat-treatment effects. These differences can be attributed to the B_2O_3 content, high concentrations giving longer 'neck' to the expansion curve."

Fig 3, shows the average coefficient of linear thermal expansion α for series I and series II base glasses. Series II base glass has a higher coefficient of thermal expansion than series I base glass at all temperatures. This point is discussed qualitatively in the light of G. A. Krestov's work⁵ on linear coefficient of expansion and on our own observation of the linear coefficient of expansion for other glasses derived from the two base glasses.

The average value of α for an ionic crystal is directly proportional to the internuclear distances (and hence on the ionic radius) and inversely proportional to the product of the charges on the cations and the anions. Hence, it is easy to understand why α is smaller for network formers like SiO_2 ($r\text{-Si}^{4+} = 4.1$ nm), B_2O_3 ($r\text{-B}^{3+} = 2.0$ nm), *etc.*, than for network modifiers like Na_2O ($r\text{-Na}^+ = 10$ nm). The addition of Na_2O , therefore, generally increases the expansion coefficient of base glass.

PbO plays double role while generally it acts as a network modifier, but under certain condition it can act as a network former also. Nevertheless, an increase in the PbO content generally increases the value of α , as is to be seen in the case of series II base glass which with its higher PbO content has a higher α than the base glass of series I.

The relative effect of Na_2O and PbO addition has to be judged not on the basis of the lower charge as well as the radius of Na^+ , but the fact that it produces only non-bridging oxygen ion and hence looses the network considerably leading to a higher value of α . This is seen in glasses (Sl No 1-2) of series IIA as Na_2O replace PbO or when Na_2O is added to the base glass of series I.

A. S. Povarenykh⁶ has indicated that SO_4^{2-} can also be treated as a network former and by using the thermochemical ionic radius given by K. B. Yatsimirskii⁷ for network forming anions, it is possible to expect that replacement of SO_4^{2-} by SiO_4^{4-} will lead to decrease in the value of α . This is seen in the case of glasses of series IIB. The thermochemical ionic radius for SO_4^{2-} ($r = 23.0$ nm) is not very different from

TABLE V
Composition (mole per cent) and thermal expansion of glasses

Sl No	SiO_2	B_2O_3	PbO	$\alpha \times 10^6 \text{ K}^{-1}$
1	50	—	50	8.6 (425-475K); 8.9 (373-673K) ^a
2	—	50	50	9.5 (293-573K) ^b
3	45	5	50	10.0 (293-573K) ^b

a—J. F. Argyle and F. A. Hummel, *Jour Amer Ceram Soc*, **43** (9) 452-457 (1960); b—Von F. Bischoff, *Glass Tech Ber*, **28** (3) 98-100 (1955)

TABLE VI
Phase separation and dilatometric softening temperature of the glasses

Code No	Phase separation characteristics	Dilatometric softening temperature (K) [± 1 K]
Series I		
Series I-base glass	Homogeneous	(T) 716
1	"	" 709
2	"	" 703
3	"	" 694
4	"	" 683
5	"	" 709
6	"	" 701
7	"	" 695
8	Non-homogeneous	(O) —
9	Homogeneous	(T) 705
10	"	" 720
11	"	" 725
12	"	" 733
Series II		
Series II-base glass	Homogeneous	(T) 713
Series II(A)		
1	Homogeneous	(T) 699
2	"	(O) 699
3	Non-homogeneous	(O) —
4	"	" —
5	Homogeneous	(T) 680
6	"	" 667
7	"	" 667
8	"	" 668
Series IIB		
1	Homogeneous	(T) 715
2	"	" 715
3	"	" 711
4	"	" 701

O=opaque; T=Transparent

that of SiO_4^{4-} ($r = 24.0$ nm), but the higher charge of the SiO_4^{4-} tetrahedra would lead to the lower value of α . This situation is made clear by a consideration of the effective anionic charge⁸ which is -1 for SiO_4^{4-} but only $-\frac{1}{2}$ for SO_4^{2-} .

In the case of replacement of SiO_2 by B_2O_3 , the single consideration of G. A. Krestov⁵ leads to ambiguity, since the thermochemical radius of BO_3^{3-} ($r=19.1$ nm) is much smaller than that of SiO_4^{4-} ($r=24.0$ nm) and so is the charge. Hence, while the radius consideration would lead to a decrease, charge consideration would lead to an increase in α . This is easily resolved when one does not consider the total charge but the effective anionic charge. The effective anionic charge for both is -1 and hence, it is radius factor that predominates and the thermal expansion decreases. However, the substitution of the -3 coordinated B^{3+} for -4 coordinated Si^{4+} , leads to non-bridging oxygen eventually loosening of structure with concomitant increase in α or no change in α (Sl No 5-8) in series IIA.

The effect of substituting the network formers in base glass (series II) varies. B_2O_3 has the maximum effect followed by SiO_2 and SO_3 .

Conclusion

With glasses of different types of network formers, the Yatsimirskii concept⁷ of thermo-

chemical ionic radius coupled with considerations of effective ionic radius leads to a reasonably good prediction of the thermal expansion behaviour.

The literature values of α (Table V) are in agreement with the obtained result, *eg*, a glass (Sl No 4, Table IV) having composition close to PbO.SiO_2 has its value equal to $10 \times 10^{-6} \text{K}^{-1}$. It is further to be seen that $\text{PbO.B}_2\text{O}_3$ ($\alpha=9.5 \times 10^{-6} \text{K}^{-1}$) has approximately the same value of α as PbO.SiO_2 ($\alpha=10.0 \times 10^{-6} \text{K}^{-1}$) is reflected in the values of α obtained for compositions (Sl No 5-8, Table III).

The dilatometric softening temperature of glasses, decrease by adding Na_2O or Na_2SO_4 in series I (Table VI) but increase by adding SO_3 . The decrease in the softening temperature is more due to Na_2O as compared to Na_2SO_4 . In series II, the substitution of Na_2O for PbO ; B_2O_3 for SiO_2 ; and SiO_2 for SO_3 decreases the softening temperature. For a fixed mole per cent substitution, *ie*, 5, the decrease in softening temperature is maximum when B_2O_3 is substituted for SiO_2 and minimum when SiO_2 is substituted for SO_3 .

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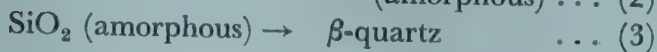
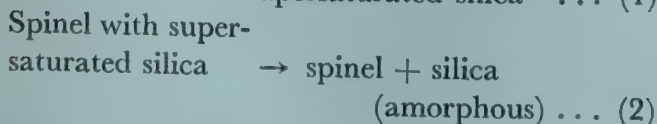
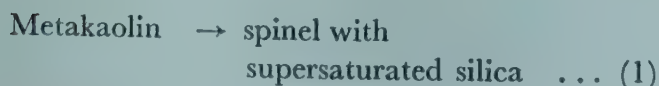
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(c) K. B. Yatsimirskii, *Izvest Akad Nauk, Otdel, Khim Nauk, SSSR* (1948), p 398.
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(Ms received October 24, 1975)

ON THE ORIGIN OF THE EXOTHERMIC PEAK IN THE THERMOGRAM OF A KAOLINITIC CLAY: SPINEL VERSUS β -QUARTZ CRYSTALLISATION*

Introduction

P. S. Nicholson and R. M. Fulrath¹ first postulated that the exothermic reaction at 980° in case of a kaolinitic clay is due to the formation of β -quartz from amorphous silica. They measured the exothermic energy by differential thermal calorimetric method of various clays to be -9 kcal/mole. G. R. Blair and A. C. D. Chaklader² along with other workers showed that spinel formation can take place under reactive hot pressing condition at lower temperatures. To understand the mechanism of the above transformation, G. R. Blair and A. C. D. Chaklader² applied Clausius-Clapeyron equation and assumed silica, as liberated, to remain in the spinel lattice while the transformation at the exothermic peak temperature would be as follows:

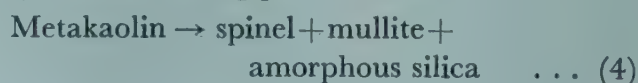


They further suggested that reactions (1) and (2) are slow, gradual and continuous process and takes place over a large range of temperature and will not reflect on the heat liberated at the exothermic reaction and silica so accumulated

at or before 980° will crystallise to β -quartz. This substantiates the contentions of P. S. Nicholson and R. M. Fulrath¹.

Applicability of Clausius-Clapeyron equation in the exothermic reaction

The present authors³, however, experimentally proved that metakaolin does not lose amorphous silica gradually and spinel is never formed from kaolinites by heating dynamically (as used in dta) below exothermic peak temperature with non-equilibrium soaking but amorphous silica is liberated only at the exothermic peak temperature with the formation of spinel and mullite. This suggests that reactions (1) and (2) as proposed by G. R. Blair and A. C. D. Chaklader² do not occur in practice, rather the only reaction taking place at 980° is,



Therefore, the application of Clausius-Clapeyron equation is not tenable in this reaction. Spinel, however, forms under special circumstances much below the exothermic peak temperature, *eg*, (a) under static heating conditions⁴; (b) reactive hot pressing².

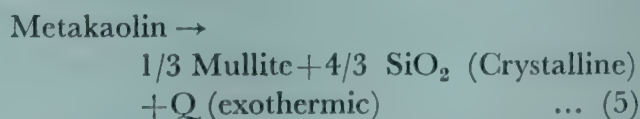
It is not justified, however, to correlate the transformation taking place (its temperatures and products) at static heating with non-equilibrium dynamic heating; secondly, at normal atmospheric pressure and temperature with reactive hot pressing conditions. Therefore, in order to explain the cause behind the exothermic reac-

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tion of a kaolinite as observed in dta curve, one should have to analyse the heated product before and after the peak temperatures of kaolin heated dynamically in the same rate as is used in dta instead of static heating or, reactive hot pressing. Few samples were collected by air quenching of an Indian kaolinite heated under dynamic heating condition at the rate of $10^{\circ}/\text{min}$. It is observed that (Table I) metakaolin lose approximately 32-35 per cent amorphous silica (estimated gravimetrically) just after 980° and it is also found that this remains more or less constant even with higher soaking time. On X-ray analysis, spinel and mullite are only observed just after the completion of the exothermic peak and the nature of the lines (1.97\AA and 1.39\AA) due to spinel, remains broad and only the lines due to mullite becomes sharper on soaking. This experiment, therefore, suggests that only at the exothermic peak temperature, spinel appears with the formation of little mullite and liberation of 32-35 per cent amorphous silica and as it remains constant which indicates that whatever transformation has taken place is complete and is not proceeding further, although sufficient heating time is allowed. From the nature of exothermic peak, amount of SiO_2 liberated and the nature of the phases so formed, suggest that the reaction is a very sharp one since these are forming from the commencement of the peak to the completion of the peak, *ie*, within a very short range of temperature (10° – 20°). Amorphous silica so liberated, remains

in the amorphous form even with long soaking time and it is very soluble in alkali and no pattern of β -quartz is obtained in X-ray analysis. Even if this amorphous silica would crystallise, the complete transformation would be about 40 per cent according to A. G. Verduch⁵, *ie*, out of 35 per cent so liberated, only 14 per cent would crystallise. Then the exothermic heat will be much less than -9 kcal/mole. Therefore, the exothermic peak is not due to the crystallisation of β -quartz. On the contrary, this rapid transformation of metakaolin into spinel and amorphous silica suggests that this reaction should also be associated with rapid evolution of heat energy.

According to R. Roy, D. M. Roy and E. E. Francis⁴ and others, metakaolin is stable in high free energy state in the range of 600° – 900° and always tends to revert to the stable assemblage of crystalline silica and mullite with evolution of energy as heat. This transition to the stable assemblage may be accomplished in one step or in several steps. Since mullite is the most stable binary crystalline phase of SiO_2 – Al_2O_3 system, its formation from kaolinite will most likely lead to the evolution of exothermic energy. This view has been verified experimentally. Also from the thermodynamic point of view of N. C. Schieltz and M. R. Soliman⁶, the most stable transformation is as follows:



Therefore, the reactions metakaolinite \rightarrow spinel + amorphous silica and spinel \rightarrow mullite + crystalline silica should not be endothermic. These are contradictory to the contention of G. R. Blair and A. C. D. Chaklader². They predict these to be endothermic reaction applying Clausius-Clapeyron equation at the reaction temperature which goes against experimental observations.

Effect of pressure on the exothermic reaction

As the density of spinel is higher than that of

TABLE I

Percentage of free SiO_2 estimated from Bhandak kaolinite heated at 980° for different periods of soaking

Period of soaking (min)	SiO_2 estimated gravi- metrically (per cent)
0	33.50
35	34.90
120	32.07
600	32.98

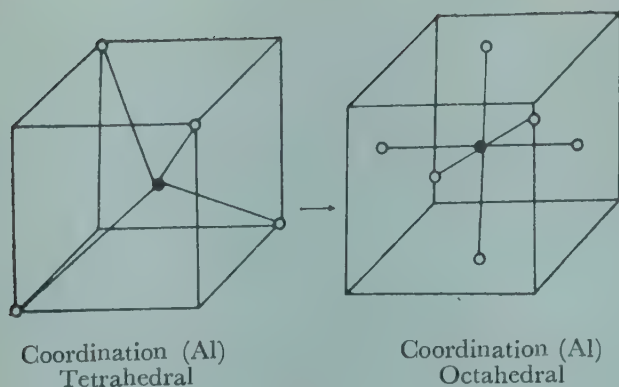


Fig 1

Accommodation of a tetrahedron and an octahedron in the same size of a cube; later shows more rigid and symmetrical arrangement formed by the application of pressure/temperature

metakaolin, the application of pressure will certainly induce the transformation of metakaolin to spinel irrespective of whether it follows a reversible or irreversible thermodynamic reaction; since in this transformation Al has changed its coordination⁷ from four in metakaolin to a more regular and stable coordination six in the cubic close packed arrangements in spinel (Fig 1).

Change in coordination from four to six will always accompany heat evolution. As the change in coordination or in other words the transforma-

tion is very rapid as observed in the above experiment, the exothermic peak must be due to the above transformation leading to the formation of spinel confirming the hypothesis of Brindley and Nakahira. G. R. Blair and A. C. D. Chaklader² obtained spinel in case of reactive hot pressing of samples, and this sample gives a dta peak of comparatively smaller magnitude than that of a sample heated at 800° without application of pressure. Present study shows that a fraction of metakaolin has undergone transformation to spinel during reactive hot pressing conditions and the remaining portion transforms at 980° giving a smaller exothermic peak as usual.

Acknowledgment

The authors thank Shri K. D. Sharma, Director of the Institute, for his kind permission to publish this research note. Thanks are also due to Prof Sadhan Bose, Calcutta University, Shri B. M. Bishui, Emeritus Scientist, CSIR and Dr B. Mukherjee, Scientist, CGCRI, for helpful discussions. One of the authors (AKC) also acknowledges the financial help provided by CSIR, India.

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(Ms received April 24, 1976)

BOOK REVIEW

High alumina refractories, edited by N. R. Sircar, published by Indian Refractory Makers' Association, 6, Netaji Subhas Road, Calcutta-700 001, India (1975), pp 208. Price Rs 25.00.

This publication contains the papers presented at a seminar on the subject held at Calcutta on May 21-22, 1973. The papers are: (i) Raw materials for high alumina refractories in India, by M. K. Roy Chowdhury; (ii) Some observations on the natural resources for high alumina refractories in India, by A. K. Bhadra, D. N. Nandi and N. R. Sircar; (iii) High alumina refractories from indigenous raw materials, by S. S. Ghose, A. K. Bose, J. R. Panda and S. Das; (iv) Development of high alumina refractories, by N. B. Chatterjee, D. N. Nandi and K. D. Sharma; (v) A comparative study of the properties of high alumina bricks made from different raw materials, by M. S. Mukherjee and H. V. B. Rao; (vi) Development of high alumina refractories from some indigenous bauxites, by G. Singh Minhas; (vii) Sintered mullite for high alumina refractories, by S. P. Banerjee and N. R. Sircar; (viii) Insight into the essential properties of high alumina refractories for superior performance, by K. P. Jhunjhunwala, M. M. Sahu and R. Misra; (ix) Significance of high temperature strength of high alumina refractories, by J. D. Panda and A. K. Tripathy; (x) Study on slag corrosion of high alumina bricks, by S. K. Mitra, B. N. Ghosh, B. Rao and K. S. Swaminathan; (xi) A study of the high temperature properties of phosphate bonded high alumina monolithics, by S. K. Mitra, B. N. Ghosh, B. Rao and K. S. Swaminathan; (xii) Some aspects of use of high alumina bricks in blast furnaces in India, by D. Roy, B. N. Majumdar, R. G. Gupta and N. Govindaswamy; (xiii) High alumina refractories—

applications, service performance and future requirements, by P. S. Sundaram, K. K. Bandyopadhyay, P. Mukhopadhyay and A. K. Ghosh; (xiv) Use of high alumina refractory bricks in rolling mill furnaces at Bhilai Steel Plant, by P. K. Aggarwal and B. K. Raut; (xv) Experience with high alumina refractories in Tata Iron and Steel Company, by T. N. Verma, B. N. Ghosh, B. Rao and K. S. Swaminathan; (xvi) Future prospects of high alumina bricks in checkers of basic open hearth furnaces at Bhilai Steel Plant, by S. K. Gupta and Maheswari Singh; (xvii) Use of high alumina bricks in the Alloy Steel Plant with special reference to vacuum degassing of steel, by D. B. Banerjee; (xviii) Technical appraisal of high alumina refractories for rotary cement kiln, by A. K. Chatterjee, A. Dasgupta and V. K. Arora; (xix) Use of alumina and high alumina refractories in fertiliser industries, by P. K. Mukherjee and B. Chatterjee; (xx) High alumina refractories in ammonia plants, by M. A. Patel and M. J. Vaidya.

The publication provides a good overview of the position of high alumina refractories in India. The book is excellently produced.

—R. L. Thakur

Mass transport phenomena in ceramics, Edited by A. R. Cooper and A. H. Heur. Plenum Publishing Corporation, 227 West 17 Street, New York, NY 10011, USA (1975). Pages 506, price US \$ 47.40.

This book comprises the papers presented at the eleventh University Conference on Ceramic Science held at Case Western Reserve University. The Conference was devoted to the subject of transport phenomena in ceramics. The papers are presented under four main divisions:

Correlation and coupling effects in diffusion in ionic materials, fast ion transport, diffusion and electrical conductivity in crystalline and glassy oxides, applications of diffusion to oxidation and other processes of current interest.

The papers incorporated in the book are: Non-random diffusion in ionic crystals, by John R. Manning; Correlation effects in ionic transport processes, by A. D. Leclaire; Coupling, cross terms, correlation and conduction, by A. R. Cooper; Irreversible thermodynamics in materials problems, by F. A. Nichols, G. P. Marino and H. Ocken; Oxygen redistribution in UO_2 due to temperature gradient, by D. D. Merchant and H. K. Bowen; The thermodynamics of diffusion controlled metamorphic processes, by G. W. Fisher; Multicomponent spinodal decomposition, by P. K. Gupta.

Microstructural aspects of optimised ion-conduction in solids, by W. Van Gool; Correlation factor and Nernst-Einstein relation in solid electrolytes, by H. Sato and R. Kikuchi; Alkali ion transport in materials of beta alumina family, by R. A. Huggins; Ionic conductivity of doped cerium oxide, by H. L. Tuller and A. S. Nowick; Low temperature oxygen transport in non-stoichiometric CeO_2 , by S. P. Ray and N. S. Nowick; Self diffusion constant measurement by continuous wave nuclear magnetic resonance, by J. Stepisnik, J. Bjorkstam and C. H. Wei.

On the interpretation of lattice diffusion in magnesium oxide, by B. J. Wuensch; High temperature electrical conductivity of aluminium oxide, by H. P. R. Frederikse and W. R. Hosler; Concentration dependent diffusion of H^+ in TiO_2 :

analysis of electronic effects in ion diffusion, by O. W. Johnson, J. W. DeFord and S. H. Paek; Measurement of chemical diffusion coefficients in non-stoichiometric oxides using solid state electrochemical techniques, by B. C. H. Steele; Comparison of atom mobility in crystalline and glassy oxides, by G. H. Frischat; Oxygen diffusion in liquid silicates and relation to their viscosity, by Y. Oishi, R. Terai and H. Ueda; Silicon and oxygen diffusion in oxide glasses, by H. A. Schaeffer; Alkali ion conductivity in fused silica, by E. M. Clausen; Cation migration in electrode glasses, by F. G. K. Bancke; A structural model of ionic and electronic relaxation in glass, by J. Aitken and R. K. MacCrone; Molecular diffusion in glasses and oxides, by J. E. Shelby.

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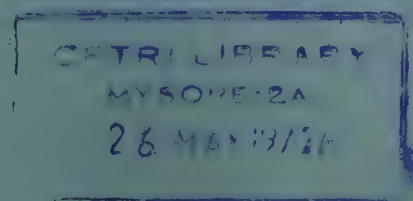
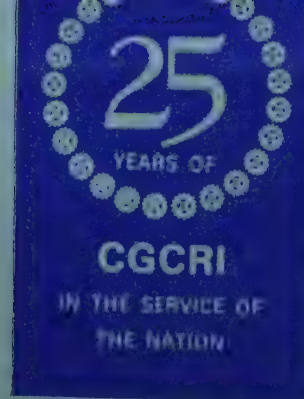
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DEPARTMENT A

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Investigation on some new sources of raw materials for glass industry: Part VI—Silica deposit from Hoshiarpur district, Punjab and quartz from Mirmi of Purulia district, West Bengal. S. K. Basu, S. K. Gupta, U. N. Nayak and S. N. Prasad, *Cent Glass Ceram Res Inst Bull*, **23** (3) 91-93 (1976).

One quartzite sample from Hoshiarpur suitable for making undecolourised glass was upgraded to grade I of IS: 488-1963 for making colourless glassware.

A sample of quartz from Mirmi was beneficiated to special grade sand after magnetic treatment for making colourless glass wares.

Studies on the formation and colour development of Cu-Zn-Sn-Cr and Cu-Mg-Sn-Cr spinels. A. K. Nandi and Purnima Sinha, *Cent Glass Ceram Res Inst Bull*, **23** (3) 93-97 (1976).

Spinel samples in the systems (i) $0.2 \text{ CuO} (1.8-x) \text{ ZnO} (1-x) \text{ SnO}_2 \cdot x \text{ Cr}_2\text{O}_3$ and (ii) $0.2 \text{ CuO} (1.8-x) \text{ MgO} (1-x) \text{ SnO}_2 \cdot x \text{ Cr}_2\text{O}_3$ were prepared for $0.2 < x < 1$. In both the systems there was a gradual contraction of the lattice for $x < 0.8$ and abrupt contraction for $x > 0.8$. This change is due to a change of cation distribution which has been correlated with the shifts in reflectance peaks and colour coordinates.

On the estimation of free silica in clays by X-ray. A. K. Chakraborty, D. K. Ghosh and B. Mukherjee, *Cent Glass Ceram Res Inst Bull*, **23** (3) 98-101 (1976).

The percentage of free silica in a number of Indian clays was determined by X-ray diffraction method. The method was very rapid and reproducibility was high. Percentage of error varied from 0.5 to 3.0.

Purification of some sand deposits around Cairo for glass making: Part I—Distribution of the iron oxide content and the nature of the sand depo-

sits. M. M. Morsi, *Cent Glass Ceram Res Inst Bull*, **23** (3) 102-106 (1976).

Most of the sand around Cairo were found suitable for manufacture of coloured glasses. The coating materials, silt clay and heavy mineral fractions represented the essential iron bearings of the sand.

Purification of some sand deposits around Cairo for glass making: Part II—Methods of purification. M. M. Morsi, *Cent Glass Ceram Res Inst Bull*, **23** (3) 106-109 (1976).

Purification of sand around Cairo consisted mainly of the removal of silt clay portion and coarse grains by simple washing and dry screening. Reduction of Fe_2O_3 content could be made by separation of the heavy minerals by froth flotation and removal of the iron coating by mechanical attrition.

A rapid method for the determination of water content in glass mixes by a waveguide. A. M. Bishai, K. N. Abd-El-Nour and F. F. Hanna, *Cent Glass Ceram Res Inst Bull*, **23** (3) 110-112 (1976).

A rapid method for estimation of water content in glass mixes has been determined. It involves measurement of the input impedance at a dielectric air boundary in a wave guide.

High temperature stable ceramic stains: Zircon-praseodymium yellow and zircon-vanadium blue. K. K. Biswas, S. K. Das, M. C. Ghose and S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **23** (3) 113-119 (1976).

The conditions leading to the formation of high temperature stable zircon-praseodymium yellow and zircon-vanadium blue stains were studied. The behaviour of these stains in different glaze compositions was also discussed in relation to the mechanism of colour formation.

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Correspondence : Editor, Central Glass and Ceramic Research Institute, Calcutta-700 032, India

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INVESTIGATION ON SOME NEW SOURCES OF RAW MATERIALS FOR GLASS INDUSTRY : PART VI—SILICA DEPOSIT FROM HOSHIARPUR DISTRICT, PUNJAB AND QUARTZ FROM MIRMI OF PURULIA DISTRICT, WEST BENGAL

S. K. BASU, S. K. GUPTA, U. N. NAYAK* AND S. N. PRASAD†

Introduction

A sample of white quartzite boulder from Hoshiarpur district of Punjab sent by the Director of Industries, Punjab, was evaluated for its suitability of glass making.

Five samples of quartz received from the West Bengal Mineral Development and Trading Corporation were also assessed for their suitability of making glass. Information regarding the location, extent of the deposit, *etc.*, was also supplied by them. These five samples were treated as part of a single sample. The Institute took up investigation on these two samples in collaboration with the respective Government Department/Organisation and the findings are given below.

White quartzite from Punjab

Location of the deposit: The deposit is located in the area of Doladikhad and Mairanadi in Hoshiarpur district of the Punjab. The nearest railway station is Garhshanker, situated at a distance of 11 km south-west of the deposit. The deposit is extended over an area of about 19,48,225 sq meters and between latitude 31°12' and 31°15' and longitude 76°12' and 76°15'. The thickness of the deposit ranges from 1 to 6.5 meters. Detailed geological investigation indicated reserves to the tune of 2.83 million tons. Total known deposits are about 4 million tons including the deposits of the adjoining areas. The deposit occurs as loose

aggregate of sand, granules, pebbles, cobbles and boulders. The deposit is accessible by motorable road throughout the year except for minor interruptions of a few days during heavy rains. There is no overburden.

Visual and microscopic examination: The sample was in the form of big pebbles, brownish in colour, and with comparatively smooth surface. It consists mainly of medium to fine quartz grains, closely packed. Minute elongated flakes of muscovites occur in between the quartz grains. Ferruginous material rarely occurs.

Crushing of lumps and chemical analysis: The quartzite lumps were crushed in a roller mill and sieved to obtain the grain size suitable for use in glass melting. It was observed that about 80 per cent of the crushed material was of suitable grain size. About 10 per cent was of coarser grain which could be recrushed to get the required size. The quantity of fine grain unsuitable for glass melting was about 10 per cent which could be used by the pottery industry. Crushing of the quartzite was found to be easier after calcination at about 1000° for 4 hours. On a commercial scale, grinding could be done in a roller mill made of chilled cast iron.

The quartzite, as received, was chemically analysed. The crushed and sieved portion (−600+125 micron IS sieve) suitable for glass melting was analysed for its iron and titania contents. Similar analysis was also done on the crushed, sieved and magnetted portion and also of the crushed, sieved, water washed and magnetted portion. These analytical results are given in Table I.

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†Emeritus Scientist, Central Glass and Ceramic Research Institute, Calcutta-700 032, India

TABLE I

Chemical analysis of white quartzite from Hoshiarpur district, Punjab

Oxides (%)	Quartzite (as received)	Quartzite (crushed and sieved)	Quartzite (crushed, sieved and magnetted)	Quartzite (crushed, sieved, washed and magnetted)
SiO ₂	98.31	—	—	—
Al ₂ O ₃	0.62	—	—	—
Fe ₂ O ₃	0.08	0.07	0.05	0.04
TiO ₂	Tr	Tr	Tr	Tr
CaO	0.17	—	—	—
MgO	0.18	—	—	—
K ₂ O	0.10	—	—	—
Na ₂ O	0.03	—	—	—
LOI	0.16	—	—	—

Quartz from West Bengal

Location of the deposit: The deposit is located in the village of Mirmi in the Balarampur block of Purulia district, West Bengal. The nearest railway station to the deposit is Urma on Adra-Chandil section of SE railway. The deposit is presently accessible only in fair weather by road. The material occurs as vein quartz and is exposed above ground on a hillock. The reserves of the deposit are estimated to be half a million tons.

Visual and microscopic examination: The sample was in lump form. It was mostly white in colour with reddish brown coating on some of

the lumps. The sample consisted solely of large irregular grains of quartz. These quartz grains were clear and often traversed by irregular fractures. The boundary between two grains were not always simple, but frequently showed sutured margins.

Preparation of sample and chemical analysis: The lumps of quartz were calcined in a furnace at about 1100°, cooled and crushed in a jaw-cum-roller crusher. The crushed material was sieved through 600 micron and 125 micron IS sieves, as generally this is the portion (—600+125 micron) used in glass industry. A representative portion of the above was chemically analysed. Another representative portion was passed through an electromagnet to remove any free iron which might have been introduced during the process of crushing. The magnetted portion was analysed for its Fe₂O₃ and TiO₂ contents. The results of the chemical analysis are given in Table II.

Conclusions

The quartzite received from Hoshiarpur district conforms to grade 3 of IS:488-1963 and is suitable for making undecolourised glass, like sheet glass and coloured glasses like green or amber glass containers for beer, and medicines. After sieving the crushed quartzite, there was slight improvement and the sample conformed to grade 2 of IS:488-1963 which was suitable for manufacture of commercial glass bottles. The crushed and sieved sample improved further on magnetic treatment but it was still within the range of grade 2 of IS : 488-1963. Bottles made after the magnetic treatment had lesser

TABLE II

Chemical analysis of Mirmi quartz

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	LOI
—600+125 micron sieved fraction before magnetizing	99.38	0.22	0.06	Tr	Tr	0.10	0.01	0.06	0.24
—600+125 micron sieved fraction after magnetizing	—	—	0.016	—	—	—	—	—	—

tint than those produced from quartzite without magnetizing. Further improvement was possible if the crushed and sieved portion was water washed and then subjected to magnetic treatment. This beneficiated the quartzite to grade 1 suitable for decolourised containerware and lampware.

The sieved fraction ($-600+125$ micron) of the sample from Mirmi, on chemical analysis, was found to contain 0.06 per cent of Fe_2O_3 and conformed to grade 2 of IS: 488-1963 for glass making sand. It would be suitable for making glassware where slight tint is permissible, like aerated water bottles. On magnetic treatment the sample was upgraded to special grade of IS: 488-1963 suitable for making high grade colourless glassware, like crystal glass tableware and decoratedware.

Summary

One sample of white quartzite from Hoshiar-

pur district, Punjab was evaluated for its suitability for glass making. The sample as received conformed to grade 3 of IS: 488-1963 suitable for making undecolourised glass. It was upgraded to grade 1 sand after water washing and magnetizing the crushed and sieved sample. The beneficiated sand then become suitable for making decolourised glassware.

A sample of quartz from Mirmi of Purulia district, West Bengal was evaluated for its use in glass industry. The quartz after crushing and sieving conformed to grade 2 of IS: 488-1963. It could be beneficiated to special grade quality of IS: 488-1963 after magnetic treatment.

Acknowledgment

The authors thank Shri K. D. Sharma, Director of the Institute, for his kind permission to publish the paper. They also thank Dr B. C. Sinha and Dr N. R. Sircar for the chemical and petrographic analyses.

(Ms received August 6, 1976)

STUDIES ON THE FORMATION AND COLOUR DEVELOPMENT OF Cu-Zn-Sn-Cr AND Cu-Mg-Sn-Cr SPINELS

A. K. NANDI AND PURNIMA SINHA*

Introduction

The basic factors controlling the nature of the absorption spectra of transition metal complexes are : (i) coordination of the ligand and symmetry of the cluster, (ii) metal ligand distance, (iii) nature of the ligand and the nature of the metal ions and (iv) the state of oxidation of the metal ions. Several combinations of the above four factors produce various shades of coloured crystals in nature.

Spinel having different cation distribution in tetrahedral and octahedral sites provide very

good scope for such colour variation. A. Ohtsuka¹ has studied the colour change in Zn-Sn and Mg-Sn systems containing Cu^{2+} , Cr^{3+} and Ni^{2+} .

In the present work Zn-Sn and Mg-Sn spinels with substitution of Cu^{2+} and Cr^{3+} in various proportions have been studied. It is expected that Zn^{2+} having a strong tetrahedral preference would tend to keep Cu^{2+} in octahedral position and Mg^{2+} having a greater octahedral preference compared to that of Cu^{2+} would tend to keep Cu^{2+} in predominantly tetrahedral position. Substitution of Cr^{3+} for Sn^{4+} should have the effect of contracting the lattice. Also, due to strong octahedral preference, Cr^{3+} would

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occupy the octahedral position and push Cu^{2+} and Mg^{2+} out of octahedral to tetrahedral position.

Experimental

Preparation of samples: Samples (Table I) having the following compositions were prepared: (1) $0.2 \text{ CuO} (1.8-x) \text{ ZnO} (1-x) \text{ SnO}_2 x \text{ Cr}_2\text{O}_3$, (2) $0.2 \text{ CuO} (1.8-x) \text{ MgO} (1-x) \text{ SnO}_2 x \text{ Cr}_2\text{O}_3$, where x was 0, 0.2, 0.4, 0.6, 0.8 and 1.

The mixtures of pure oxides of required proportions were ground in acetone medium. Pressed discs of the samples were fired at 1150° for 3-4 hours. The samples were reground and refired at the same temperature.

X-ray analysis: X-ray powder photographs were taken with Cu K_α radiation by 11.46 cm dia Philip's camera. Lattice constants were determined by extrapolation method.

Reflectance spectra: The reflectance spectra of the samples were taken in automatically recording Hardy Spectrophotometer.

Colour coordinates: ICI trichromatic colour coordinates were measured by Gardener Multi-purpose Reflectometer.

Results and discussions

The reflectance spectral curves of $0.2 \text{ CuO} (1.8-x) \text{ ZnO} (1-x) \text{ SnO}_2 x \text{ Cr}_2\text{O}_3$ for $x=0, 0.2, 0.4, 0.6, 0.8$ and 1, in the range $380 \text{ m}\mu$ to $700 \text{ m}\mu$ is given in Fig 1. X-ray data indicated that single spinel was formed for all these values of x .

For $x=0$, the cation distribution is represented as $\text{Zn} [0.8 \text{ Zn} 0.2 \text{ Cu} \text{ Sn}]$, where [] indicates octahedral coordination. The absorption² beyond $700 \text{ m}\mu$ with a peak around $800 \text{ m}\mu$ was due to octahedral Cu^{2+} . Absorption at $390 \text{ m}\mu$ was observed for $x=0$ and $x=0.2$ in this system.

For $x=0.2$, the peak for 6-coordinated Cr^{3+} appears near $630 \text{ m}\mu$ and $470 \text{ m}\mu$. A violet shift of these peaks to $610 \text{ m}\mu$ and $400 \text{ m}\mu$ occurs for $x=0.4$ due to the octahedral site which is due

TABLE I

Variation of colour and lattice constants with variation of composition in Cu-Zn-Sn-Cr and Cu-Mg-Sn-Cr systems

No	Composition	Cu-Zn-Sn-Cr system				Colour	Lattice constant (Å)
		x	y	$\lambda_{\text{DM}}(\text{m}\mu)$	Y (%)		
1	$\text{Cu}_{0.2} \text{ Zn}_{1.8} \text{ Sn}$	0.35	0.35	580	70.8	Yellow orange	8.668
2	$\text{Cu}_{0.2} \text{ Zn}_{1.6} \text{ Sn}_{0.8} \text{ Cr}_{0.2}$	0.35	0.39	570	32.8	Yellowish green	8.622
3	$\text{Cu}_{0.2} \text{ Zn}_{1.4} \text{ Sn}_{0.6} \text{ Cr}_{0.4}$	0.35	0.39	570	29.2	Yellowish green	8.542
4	$\text{Cu}_{0.2} \text{ Zn}_{1.2} \text{ Sn}_{0.4} \text{ Cr}_{0.6}$	0.34	0.37	568	24.02	Yellow green	8.530
5	$\text{Cu}_{0.2} \text{ Zn} \text{ Sn}_{0.2} \text{ Cr}_{0.8}$	0.33	0.38	563	17.8	Yellowish green	8.369
6	$\text{Cu}_{0.2} \text{ Zn}_{0.8} \text{ Cr}$	—	—	—	—	Black	8.340
Cu-Mg-Sn-Cr system							
7	$\text{Cu}_{0.2} \text{ Mg}_{1.8} \text{ Sn}$	0.37	0.37	575	65.2	Yellow	8.652
8	$\text{Cu}_{0.2} \text{ Mg}_{1.6} \text{ Sn}_{0.8} \text{ Cr}_{0.2}$	0.33	0.34	570	30.5	Greenish yellow	8.594
9	$\text{Cu}_{0.2} \text{ Mg}_{1.4} \text{ Sn}_{0.6} \text{ Cr}_{0.4}$	0.35	0.36	575	21.6	Greenish yellow	8.582
10	$\text{Cu}_{0.2} \text{ Mg}_{1.2} \text{ Sn}_{0.4} \text{ Cr}_{0.6}$	0.32	0.36	563	18	Yellowish green	8.546
11	$\text{Cu}_{0.2} \text{ Mg} \text{ Sn}_{0.2} \text{ Cr}_{0.8}$	0.31	0.33	555	14	Green	8.349
12	$\text{Cu}_{0.2} \text{ Mg}_{0.8} \text{ Cr}$	0.30	0.33	540	10	Green	8.342

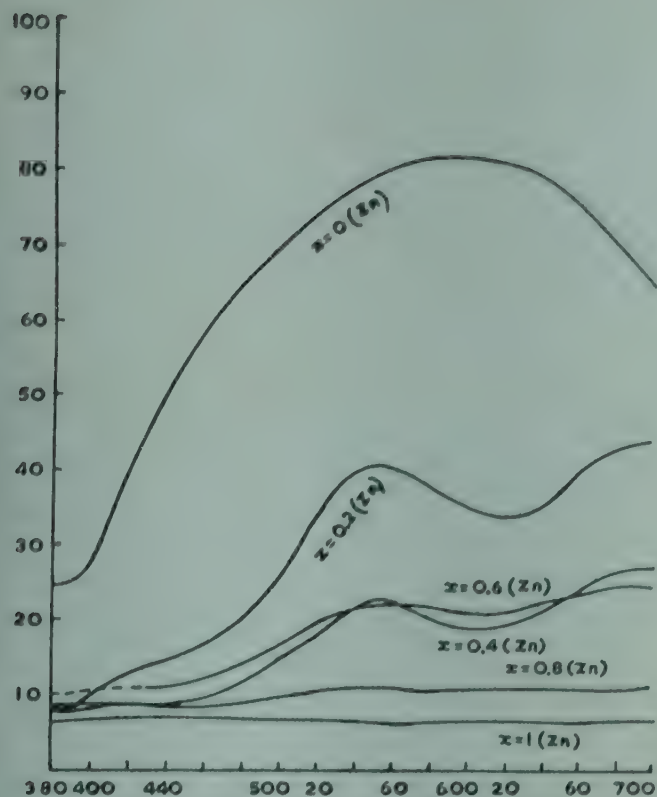


Fig 1

Reflectance spectral curves of 0.2 CuO (1.8-x) ZnO(1-x) SnO₂ xCr₂O₃ for x=0, 0.2, 0.4, 0.6, 0.8 and 1 in the range 380-700 mμ

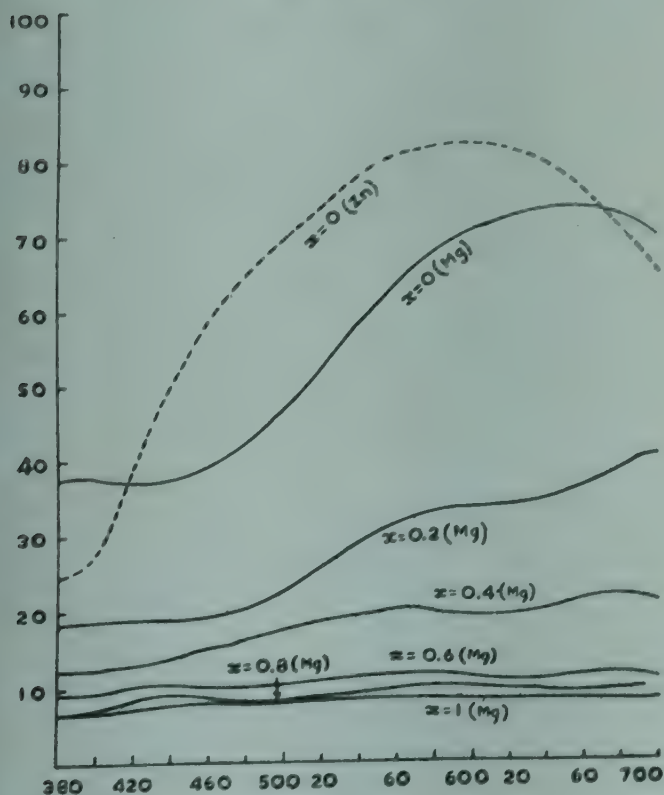


Fig 2

Reflectance spectral curves for 0.2 CuO(1.8-x)MgO(1-x) SnO₂ xCr₂O₃ for x=0, 0.2, 0.4, 0.6, 0.8 and 1

to the substitution of Sn⁴⁺ ($r=0.74\text{\AA}$) by Cr³⁺ ($r=0.65\text{\AA}$). Such shift is expected from crystal field theory. For $x > 0.4$ the Cr³⁺ peaks and other peaks due to Cu²⁺ become indistinguishable. This may be due to interference between Cr³⁺ and Cu²⁺ spectra in the system.

Fig 2 gives the spectra for 0.2 CuO (1.8-x) MgO (1-x)SnO₂ xCr₂O₃ for x=0, 0.2, 0.4, 0.6, 0.8 and 1. X-ray data indicated that single spinel was formed in all the cases. In this system a part of Cu²⁺ was expected to be in the tetrahedral coordination. Since the octahedral preference of Mg²⁺ is not much greater than that of Cu²⁺, both Cu²⁺ and Mg²⁺ would perhaps be distributed in the two sites with Cu²⁺ predominantly in the tetrahedral site. Thus the distribution would be as follows: y Cu (1-y) Mg [(0.8+y-x)Mg (0.2-y)Cu (1-x)Sn xCr₂], where maximum value of $y=0.2$.

Comparison of the spectra (Fig 3) of Zn and Mg systems for x=0 shows a distinctly different character. In the Mg-system the absorption peak at 390 mμ is absent. A broad absorption

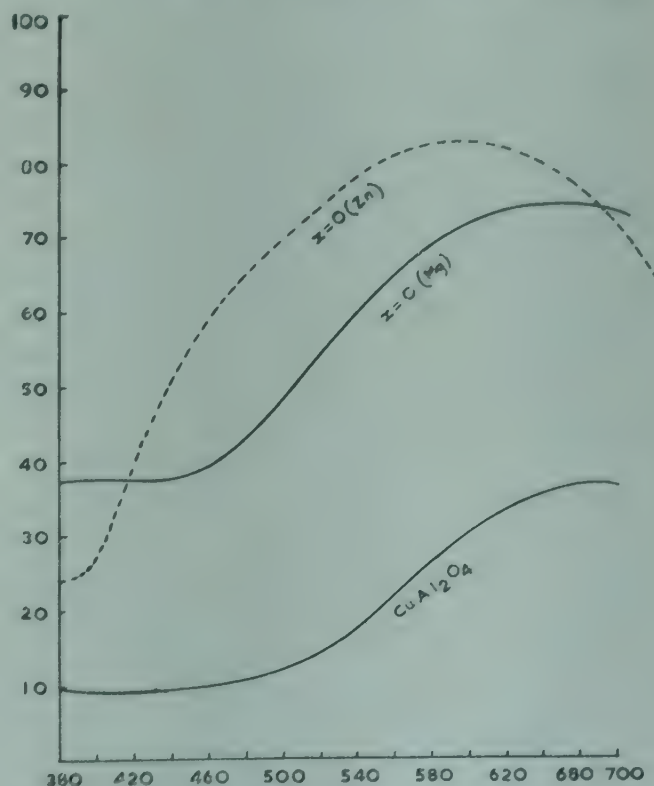


Fig 3

Reflectance spectral curves of Zn and Mg-system (x=0) compared with that of CuAl₂O₄

band up to $460\text{ m}\mu$ is observed, where there is a broad reflectance in the Zn-system. With introduction of Cr^{3+} in the lattice this peak is masked by the $460\text{ m}\mu$ Cr^{3+} peak. The bend of the curve above $700\text{ m}\mu$ is less pronounced compared to that of Zn-system indicating the presence of smaller proportion of octahedral Cu^{2+} in the Mg-system compared to that of Zn-system. Flat Cr^{3+} peaks around $460\text{ m}\mu$ and $630\text{ m}\mu$ appears for $x=0.2$ in the Mg-system. Violet shift of these peaks with concentration of Cr^{3+} could not be detected. Around $x=0.8$ and 1, the curves become almost parallel to the base line.

In Fig 3, the spectral curve with $x=0$ in the Mg-system has been compared with that of CuAl_2O_4 , where a part of Cu^{2+} is in tetrahedral coordination. The cation distribution is given by 0.6 Cu, 0.4 Al [0.4 Cu, 1.6 Al]³. The similarity of nature of the curves indicate that in the Mg-system, a part of Cu^{2+} is in tetrahedral coordination. There is indication of the $800\text{ m}\mu$ peak due to octahedral Cu^{2+} in both Zn and Mg-system. The absence of absorption around $460\text{ m}\mu$ in the Zn-system for $x=0$ indicates the absence of tetrahedral Cu^{2+} in the system. No theoretical justification on the basis of ligand field theory could be obtained for $390\text{ m}\mu$ band for octahedral Cu^{2+} and $460\text{ m}\mu$ band for tetrahedral Cu^{2+} . But from the literature on experimental work recorded for other systems, it seems that the peaks in these systems are associated with octahedral and tetrahedral Cu^{2+} respectively. R. Pappalardo⁴ observed a peak near $22,000\text{ cm}^{-1}$ ($455\text{ m}\mu$) for Cu^{2+} in ZnO (tetrahedral Cu^{2+}), which he associated with Fe^{3+} impurity or some other mechanism. L. Helmholtz and R. F. Kruk⁵ observed for Cs_2CuCl_4 a peak in the same position which may be due to Cl ligand. But the presence of a band in the same position in CuAl_2O_4 , Cu-Mg-Sn oxide spinel and Cu^{2+} in ZnO indicates that the peak is also a characteristic of tetrahedral Cu^{2+} in oxides.

O. Schmidt DuMont⁶ observed a charge transfer band at $350\text{--}270\text{ m}\mu$ in $x\text{Cu} (1-x)$

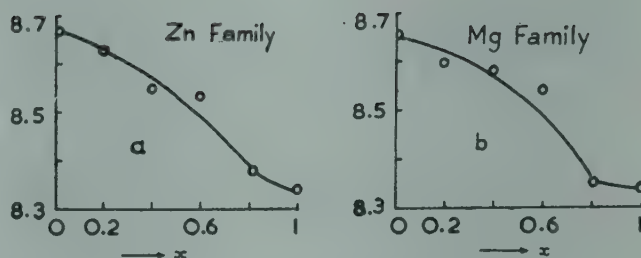


Fig 4
Variation of lattice constant with x

MgO . The $380\text{ m}\mu$ peak in the Zn-system seems to be the similar peak. Since in Zn-system Cu^{2+} would be in the octahedral position, as the case should be in Cu^{2+} in MgO , $460\text{ m}\mu$ band in the Mg-system might also be the shifted position of the same charge transfer band.

The variation of lattice constant with x is given in Fig 4. A gradual contraction of the lattice is observed upto $x=0.8$, where a sharp change of slope of the curve occurs. This seems to be the effect of migration of Cu^{2+} from six-fold to four-fold coordination around $x=1$. In case of Zn-system the whole of Cu (0.2 mole) is replaced by Cr^{3+} resulting in a contraction of the octahedral site. Also, simultaneous replacement of Zn^{2+} by Cu^{2+} in tetrahedral position produces a tetrahedral site contraction. In Mg-system with distribution: $y\text{Cu} (1-y)\text{Mg} [(0.8+y-x)\text{Mg} (0.2-y)\text{Cu} (1-x)\text{Zn} x\text{Cr}_2]$, whatever be the proportion of Mg^{2+} and Cu^{2+} in octahedral position, whole of Mg^{2+} and Cu^{2+} would be migrated to tetrahedral position for $x=1$. The nature of change of slope in both the systems is similar, indicating that the removal of a part of Cu^{2+} and a part of Mg^{2+} having a comparable ionic radius of 0.70 and 0.78 respectively from the octahedral position has similar effect on lattice dimension as the migration of Cu^{2+} alone in the Zn-system. The change is slightly more pronounced in the Zn-system which may be due to the added effect of tetrahedral contraction as a result of replacement of Zn^{2+} by Cu^{2+} .

Colour coordinate data are given in Table 1. The colour of the samples in the Zn-system varied from yellow orange ($x=0$) to various

shades of green to black. In the Mg-system the colour changed from yellow ($x=0$) to various shades of green. There is slight variation of colour between the two systems, which seems to be due to the difference in distribution of Cu^{2+} in the two systems. Change in colour with sharp change of lattice constant is more pronounced in the Zn-system, where there is greater change of slope of the curve compared to that of Mg-system. The colour becomes gradually darker with concentration of Cr^{3+} in both the cases. The effect of change of coordination of Cu^{2+} on colour was masked by the effect of octahedral Cr^{3+} in the systems. Substitution of Al^{3+} for Cr^{3+} in the lattice would perhaps indicate the effect of change of cation distribution of Cu^{2+} with change of concentration of Zn^{2+} and Mg^{2+} on colour development more distinctly.

Summary

Spinel samples in the system : (i) $0.2\text{CuO} (1.8-x)\text{ZnO} (1-x)\text{SnO}_2 x\text{Cr}_2\text{O}_3$ and (ii)

$0.2\text{CuO} (1.8-x)\text{MgO} (1-x)\text{SnO}_2 x\text{Cr}_2\text{O}_3$ were prepared for $x=0, 0.2, 0.4, 0.6, 0.8$ and 1 , by firing the mixture of oxides at 1150° . Reflectance spectra of the samples indicated a difference in cation distribution between the two systems. In both the cases (i) and (ii) there was a gradual contraction of the lattice with increasing value of x and a sudden change from $x=0.8$ to $x=1$. This seemed to be due to a change of cation distribution for $x > 0.8$. The colour of the samples changed from yellow orange through various shades of green to very dark green and black. A slight change in colour was observed between systems (i) and (ii) probably due to variation of cation distribution in the two systems.

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ON THE ESTIMATION OF FREE SILICA IN CLAYS BY X-RAY†

A. K. CHAKRABORTY, D. K. GHOSH AND B. MUKHERJEE*

Introduction

Estimation of free quartz in clays is often necessary especially when the clays are used as ingredients for production of ceramic materials.

Atma Ram, B. M. Bishui and R. N. Dhar¹ had estimated quantitatively the presence of free silica in a number of Indian clays by infrared absorption technique. The percentage of quartz in Indian clays had earlier been determined by Atma Ram, J. C. Banerjee and D. N. Nandi² using dta method. There are various other methods by which quantitative analysis of phases is possible. Powder X-ray diffraction method has a distinct advantage over the others since each phase produces its characteristic pattern independently of others and the intensity of each component pattern is proportional to the amount present. M. E. Cosgrove and A. M. A. Sulaiman³ had reported the estimation of quartz in sedimentary rocks by X-ray diffraction procedure. In the present paper, authors have made an attempt to estimate the amount of quartz in a number of mixtures containing different percentages of pure quartz and kaolinite by X-ray powder diffractometry following the procedure of J. Leroux, D. H. Lennox and K. Kay⁴. Finally the percentage of quartz in a number of Indian clays has been estimated.

Basic aspects of absorption in quantitative analysis

L. Alexander and H. P. Klug⁵ derived the following formula expressing the value of intensity, I_1 , diffracted at a definite Bragg angle

by a crystalline component 1 in association with other crystallites in an ideal powder

$$I_1 = \frac{K_1 X_1}{\rho_1 [X_1 (\mu_1^* - \mu_2^*) + \mu_2^*]} \quad \dots (1)$$

This on further simplification becomes

$$I_1 = \frac{K_1 X_1}{\rho_1 [\mu_1^* X_1 + \mu_2^* X_2]} \quad \dots (2)$$

Where, K_1 is a constant which depends upon the nature of the component 1 and geometry of the apparatus; X_1 is weight fraction of component 1; μ_1^* is the mass absorption coefficient of component 1; ρ_1 is the apparent density of component 1; μ_2^* is the mass absorption coefficient of the matrix; and X_2 is the weight fraction of the matrix.

Expressing the mass absorption coefficient of the powder sample as μ_s^* , equation (2) reduces to

$$I_1 = \frac{K_1 X_1}{\rho_1 \mu_s^*} \quad \dots (3)$$

When the sample consists of only one component in the pure form, equation (3) can be written as

$$(I_1)_0 = \frac{K_1}{\rho_1 \mu_1^*} \quad \dots (4)$$

Where, $(I_1)_0$ is the intensity of a single component, *ie*, when $X_1=1$. Combining equations (3) and (4) we get

$$X_1 = \frac{I_1}{(I_1)_0} \frac{\mu_s^*}{\mu_1^*} \quad \dots (5)$$

When $\mu_s^* = \mu_1^*$, equation (5) becomes $X_1 = I_1/(I_1)_0$. In other words, when the absorbing power of the component whose percentage is to be determined is same as that of the entire

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mixture, then the ratio of the intensities $I_1/(I_1)_0$ is a direct measure of the concentration. This is only possible in case of polymorphs whose mass absorption coefficient are similar, *eg*, polymorphs of silica, quartz, cristobalite and tridymite.

Deduction of expression for absorption ratio

General equation of transmission of X-rays through a sample when placed perpendicularly to the direction of X-rays is given by

$$T_s = T_0 \exp(-\mu_s^* \cdot \rho_s \cdot t_s) \quad \dots (6)$$

where, T_0 is the intensity of the incident X-ray beam per unit area; T_s is the intensity of the transmitted X-ray beam per unit area; μ_s^* is the mass absorption coefficient of the sample; ρ_s is the apparent density of the sample; and t_s is the thickness of the sample through which X-rays travel.

Similarly, when the sample consists of only one component in the pure form, we have

$$T_1 = T_0 \exp(-\mu_1^* \cdot \rho_1 \cdot t_1) \quad \dots (7)$$

Taking log of equations (6) and (7) and combining them, we have

$$\frac{\mu_s^*}{\mu_1^*} = \frac{\log_e (T_s/T_0)}{\log_e (T_1/T_0)} \frac{\rho_1 t_1}{\rho_s t_s} \quad \dots (8)$$

Substituting the value of μ_s^*/μ_1^* from equation (8) in equation (5), we get

$$X_1 = \frac{I_1}{(I_1)_0} \frac{\log_e (T_s/T_0)}{\log_e (T_1/T_0)} \frac{\rho_1}{\rho_s} \quad \dots (9)$$

when $t_1 = t_s$.

μ_s^*/μ_1^* was also calculated theoretically from the equation

$$\mu_s^* = \mu_1^* X_1 + \mu_2^* X_2 \quad \dots (10)$$

where, μ_s^* is the mass absorption coefficient of the mixture, μ_1^* and μ_2^* is the mass absorption coefficient of components 1 and 2; X_1 and X_2 is the weighed fractions of the components 1 and 2 respectively.

Experimental

Bhandak clay (kaolin) was centrifuged repeatedly and finally examined for the presence of quartz by X-ray diffraction method, both photographically and by taking traces in the diffractometer. Optical grade quartz was ground in an agate mortar and the powdered sample was passed through a 325 mesh sieve. Weighed amounts of Bhandak clay and quartz were mixed in an agate mortar in presence of acetone for about an hour. In this way, several number of samples containing different amount of quartz were prepared.

Dried sample was then packed into the cavity ($2 \times 1 \times 0.1$ cm) of a diffractometer sample holder kept flat over a glass slide. Excess sample was removed by the edge of a glass slide. Care was taken to note that the powder surfaces were as plane as possible and were in line with the sample holder, *ie*, the thickness of the sample packed was equal to the thickness of the sample holder.

Philips X-ray crystallographic unit (PW-1010) fitted with a copper target and Philips wide range goniometer (PW-1050) provided with a scintillation counter were used. The tube was run at 30 kV 20 milli amphere. $I_1/(I_1)_0$ was determined by comparing the diffracted intensity of nickel filtered CuK_α radiation from 101 plane ($d=3.34$ Å) of quartz in the mixtures with that of the pure quartz sample.

The mechanical register provided with the diffractometer was run between 2θ , 26.4° - 26.9° and the total number of counts was proportional to the area of the scanned portion of the pattern. This was inclusive of background counts. Hence, the background was subtracted by recording the counts in a region adjacent to the line of the same width as the scanned line.

For the absorption measurements, the sample holders were kept at right angles to the incident X-ray beam and the intensity of the transmitted beam was counted for a fixed interval of time. The sample holders were weighed before and after packing of the samples. Difference in weight gave the amount of sample taken. Ratio

TABLE I

Concentration of quartz as actually taken and experimentally observed in Bhandak clay and quartz mixture

Actual concentration of quartz in clay-quartz mixture (%)	Experimentally obtained concentration of quartz before mass absorption correction is made	Experimentally obtained values of μ_s^*/μ_1^*	Values of μ_s^*/μ_1^* as read off from the graph (Fig 1)	Experimentally obtained concentration of quartz in clay-quartz mixture after mass absorption correction (%)	Percentage error
3.15	3.243	0.9473	0.960	3.112	-1.206
7.04	7.129	0.9204, 0.9371	0.962	6.858	-2.585
18.05	18.090	0.9661, 0.9475	0.968	17.51	-2.990
19.75	20.460, 20.530	0.9513	0.970	19.85, 19.92	+0.5063, +0.8606
25.00	25.930, 25.740, 25.350	0.9654, 0.9727	0.971	25.18, 25.00, 24.63	+0.7201, 0, -1.48
53.65	54.360, 54.11	0.9893	0.978	53.16, 52.91	-0.9133, -1.379
60.94	60.70, 61.24	0.9607	0.980	59.48, 60.02	-2.396, +1.51
78.23	79.98	0.9870	0.990	79.16	+1.189

of the mass absorption coefficient (μ_s^*/μ_1^*) was found out from equation (8).

Results and discussions

The concentration of quartz as actually taken in the mixture of Bhandak clay and quartz and as experimentally observed is given in Table I. The results show an excellent agreement between the actual concentration of quartz in a number of clay-quartz mixture with experimentally determined quartz concentration before and after the application of correction factor due to mass absorption. In this case mass absorption does not affect very much as the

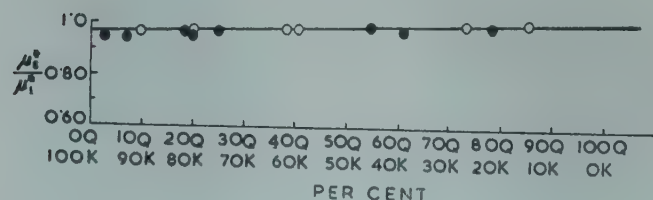


Fig. 1

μ_s^*/μ_1^* vs concentration. ○—theoretical values; ●—experimental values

TABLE II

Free silica determined by X-ray diffraction method in a number of Indian clays

Name of clay	Quartz after correction (%)
Bansi clay (white) recentrifuged	9.23 9.32
Rajhava fine clay (as such)	38.88 38.98
Than clay (as such)	28.05 27.50 28.74
Jubbulpur clay (as such)	21.36 21.35
Than clay (washed at CGCRI)	16.31 16.72
Beldanga clay (as such)	15.37 15.21

densities as well as mass absorption coefficients are more or less of the same order in the case of

quartz and clay. But where the densities and mass absorption coefficients of the component, whose concentration is sought, will widely vary from that of the matrix composition, the correction term will become important. Therefore, care should be taken to estimate the mass absorption coefficient. In Fig 1, theoretical values of μ_s^*/μ_1^* and experimentally obtained values of μ_s^*/μ_1^* vs concentrations are plotted. The deviations observed are due to experimental error. The percentage error estimated in each case shows that the variation lies within the limit of 0.5 to 3. This shows that the method of determination of free quartz by X-ray diffraction procedure is a fairly accurate one.

Free silica (quartz) contents in several Indian clays are given in Table II.

Summary

The percentage of free silica in a number of Indian clays was determined by X-ray diffraction method. The method was very rapid and reproducibility was high. Percentage of error varied from 0.5 to 3.0.

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PURIFICATION OF SOME SAND DEPOSITS AROUND CAIRO FOR GLASS MAKING: PART I—DISTRIBUTION OF THE IRON OXIDE CONTENT AND THE NATURE OF THE SAND DEPOSITS

M. M. MORSI*

Introduction

Purification of sands for the purpose of glass manufacture depends largely on the form in which iron is present. The different forms in which iron may exist in a sand deposit are: (a) bound with argillaceous admixtures, (b) as a component of heavy minerals, (c) as a film adhering tightly to the surface of quartz grains, (d) as inclusions within the quartz grains, and (e) as a part of some light silicate minerals associated with the sand.

In the present work, sand deposits from ten localities around Cairo, *ie*, those from Almaza, Manshiat El-Bakri, El-Nahadein, El-Nassr City 7th, Liblaba, Maadi, Cairo-Suez Road, El-haram, Helwan and Kafr El-Ilw were studied.

Experimental

Preparation of samples for examination: In each locality, the deposits were explored and the different hills and quarries scattered in the area were sampled^{1,2}. The samples collected were 12 to 20 in number for each locality. They were subjected to a preliminary study based on particle size and colour of sand to decide whether the samples were of similar type. Samples of the same type (mostly found to be present in close distance) were subjected to thorough mixing using equal quantities. The mixed sample was taken to be representative for the main deposits present in the same locality. The total number of representative samples obtained from the ten localities studied were sixteen in number (Table I).

For the studies, representative fractions were

obtained using the quartering method³. The fractions prepared for chemical analysis and for iron oxide determination were ground in an agate mortar to pass through the 200 mesh sieve (0.074 mm).

On each sample different components of the sand, iron oxide in the different size fractions, and the different forms of iron oxide content of the sand were determined.

Silicate analysis: The determination⁴⁻⁷ of the different components of the untreated sands was carried out on 1.0-1.5 gm of the ground and dried samples. The chemical composition of the sands was expressed in terms of silica, alumina, ferric oxide, calcium oxide, magnesium oxide, potassium oxide, and volatile materials (Table II).

Estimation of iron oxide

About 0.6-0.7 gm of the ground and dried sample was decomposed by HF acid in a platinum dish and dissolution was carried out using HCl (1:1). Thioglycollic acid in presence of 10 per cent tartaric acid was added to the iron solution in an ammoniacal medium. The iron oxide was determined colorimetrically using Beckman DR spectrophotometer at 540 nm.

Distribution of iron in the different size fractions: The relation between different sizes of the sand and the iron oxide content was studied in the sample numbers 3, 5b, 6, 7 (mixed sample of nos 7a, 7b and 7c) and 10. Sand nos 6 and 7 had relatively low iron content; nos 3, 5b had intermediate and 10 had high iron content. Mechanical screening was carried out on the chosen samples and the iron content of each fraction was determined.

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TABLE I

Locality, sample numbers, geographic position and stratigraphic unit of the studied sands

Geographic position	Locality	Locality number	Sample number	Stratigraphic unit
East of Cario	Almaza	2	2	Oligocene
	Manshiat El-Bakri †	3	3	
	El-Nahadein	4	4a, 4b	
	El-Nassr City 7th	5	5a, 5b, 5c	
	Liblaba	6	6	
	Bir El-Fahm (Maadi)	7	7a, 7b, 7c	
West of Cairo	Cairo-Suez Road	1	1	Non-marine miocene
	El-Haram (Pyramids)	10	10	Pliocene-recent
South of Cairo	Helwan	8	8	Pleistocene-recent
	Kafr El-Ilw	9	9a, 9b	

† The name Manshiat El-Bakri given to locality number 3 was adopted due to its nearness to Manshiat El-Bakri district in Cairo

TABLE II

Chemical composition of the sand samples studied

Sample number	SiO ₂ (%)	R ₂ O ₃ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	LOI (%)
2	95.7	2.0	0.476	1.6	0.7	0.1	0.8	0.6	0.4
3	94.8	1.8	0.315	1.5	1.1	0.9	0.9	0.2	0.3
4a	94.6	2.8	0.244	2.6	0.5	0.8	0.1	0.3	0.8
4b	94.7	3.0	0.391	2.6	0.3	0.9	0.1	0.3	0.6
5a	95.9	2.1	0.532	1.5	0.8	0.2	0.3	0.4	0.6
5b	94.6	2.6	0.394	2.2	0.6	0.9	0.2	0.3	0.5
5c	94.7	2.5	0.459	2.0	0.9	0.3	0.3	0.6	0.7
6	95.5	2.3	0.280	2.0	0.9	0.4	0.2	0.3	0.4
7a	96.5	1.7	0.254	1.4	0.5	0.4	0.2	0.2	0.5
7b	96.1	1.7	0.263	1.5	0.7	0.5	0.2	0.2	0.8
7c	96.0	1.8	0.277	1.6	0.6	0.4	0.2	0.2	0.6
1	96.6	1.4	0.451	0.9	0.7	0.2	0.6	0.6	0.3
10	92.6	3.3	0.899	2.4	1.9	0.5	0.4	0.6	0.7
8	92.6	3.9	0.902	3.1	0.9	0.8	0.6	0.8	0.3
9a	93.4	3.2	0.442	2.7	0.4	1.3	0.6	0.9	0.4
9b	94.0	2.7	0.493	2.2	1.1	0.7	0.5	0.9	0.3

The iron present in the sand fractions were determined by: (i) Separation of the silt-clay fractions: After washing⁸, the silt-clay portion was removed and the sand was dried and the iron oxide was determined. The difference in the iron content of the original sand and that of the sand after washing was considered to be of that present in the silt-clay fraction.

(ii) Heavy mineral separation, using bromoform (sp gr 2.85): The light fraction was washed, dried and its iron content was determined. The difference in the iron content of the light fraction and that of the washed sand was considered as the iron present in the heavy minerals associated with the sand.

(iii) Chemical treatment of the light fraction: The light fraction was chemically treated to remove the coating materials adhering tightly to the quartz grains which may be hematitic or limonitic materials.

The sand was completely wetted in 5 per cent caustic soda solution and heated at 160° to dryness. Thus the ferric oxide present was converted to sodium ferrite. Hydrolysis with water followed by washing removed the regenerated iron oxide. The successive treating with 2 per cent sulphuric acid removed the remaining iron.

Results and discussion

The results of analyses of the sixteen representative samples are recorded in Table II. The maximum percentage of silica (96.0-96.6) was found in samples of Cairo-Suez Road and Maadi. The minimum percentage (92.6-94.0) was in samples of El-Haram, Kafr El-Ilw and Helwan. The samples had iron oxide ranging between 0.244 and 0.532 per cent. The Fe_2O_3 was comparatively low (0.244-0.280 per cent) in Maadi, Liblaba and El-Nahadein sands, and higher (0.476-0.902 per cent) in samples of Almaza, Kafr El-Ilw, El-Nassr City 7th, El-Haram and Helwan.

The distribution of Fe_2O_3 in the different size fractions of the sands is given in Table III. Iron was generally concentrated in the fine particles, less than 0.1 mm diameter, and in the

coarse ones, greater than 0.8 mm diameter. The removal of these fractions would reduce greatly the amount of Fe_2O_3 in the sands when used in the manufacturing of glass.

The results obtained from the studies carried out on the distribution of the iron oxide content of the sand samples are given in Table IV.

The sand after the removal of the silt-clay particles by the washing process could be classified into three types:

(i) Sand in which the iron oxide was mainly concentrated in the heavy minerals (sample nos 1, 4b, 7b, 8 and 9a), it ranges between 31.77 per cent in heavy minerals associated with sand (9a) and 51.04 per cent with number 1 of the total iron oxide.

(ii) Sand in which the Fe_2O_3 was mainly concentrated in the coating materials (sample nos 2, 3, 4a, 5a, 5b, 5c, 6, 7a, 7c, 9b and 10),

TABLE III

Distribution of iron oxide in the different size fractions of sample numbers 2, 5b, 6, 7 (mixed sample) and 10

Fraction remained on sieve with aperture (mm)	Fe_2O_3 content in the fraction of sample number (%)				
	2	5b	6	7	10
2.0	0.338				
1.0	0.183			0.492	
0.8	0.164	0.169	0.121		0.230
0.63	0.046	0.141	0.111	0.425	0.245
0.50	0.229	0.172	0.146	0.414	0.286
0.40	0.173	0.199	0.191	0.298	0.334
0.315	0.162	0.231	0.242	0.252	0.558
0.25	0.181	0.262	0.316	0.209	0.842
0.20	0.215	0.329	0.363	0.367	1.074
0.16	0.455	0.510	0.430	0.341	1.480
0.10	1.197	1.065	0.804	1.102	2.427
— 0.10	3.153	1.586	1.304	1.910	3.812

TABLE IV

Iron oxide present in the sand after each corresponding operation

Sample number	Fe ₂ O ₃ present in the original sand (%)	Fe ₂ O ₃ (%) present after		
		Washing	Separation of the heavy minerals	Chemical treatment
2	0.476	0.371	0.342	0.022
3	0.315	0.222	0.138	0.012
4a	0.244	0.202	0.180	0.057
4b	0.392	0.230	0.103	0.004
5a	0.532	0.355	0.219	0.013
5b	0.394	0.224	0.213	0.013
5c	0.459	0.361	0.336	0.014
6	0.280	0.250	0.169	0.005
7a	0.254	0.180	0.115	0.017
7b	0.263	0.210	0.103	0.023
7c	0.277	0.164	0.134	0.029
1	0.451	0.434	0.204	0.054
10	0.899	0.765	0.553	0.029
8	0.902	0.736	0.306	0.178
9a	0.442	0.283	0.143	0.084
9b	0.493	0.445	0.553	0.029

it varied between 37.90 per cent for sand 7c and 70.28 per cent for sand 5c.

(iii) Sand in which the Fe₂O₃ was more or less equally concentrated in the heavy minerals

and the coating materials (sample nos 3, 4b, 5a, 7a and 7b).

From the iron oxide content point of view, most of the sands are suitable for the manufacture of coloured glass and amber glassware. Maadi and Liblaba sands are suitable for the manufacture of white colourless glass after the removal of the fine and coarse particles. Cairo-Suez Road sand can be used for the same purpose after the removal of the heavy minerals.

It appears, therefore, necessary to apply some methods of purification of these sands with a view to removing part or all the undesirable iron oxide.

Summary

Sand deposits from ten localities around Cairo were studied. Most of the sand deposits were found to be suitable for manufacturing of coloured and amber glasses. The iron oxide was mainly concentrated in the silt-clay and to a less extent in the large particles. However, the coating materials, the silt-clay particles and the heavy minerals represent the essential iron bearings. After washing, three types of the sand deposits can be distinguished: (i) those in which Fe₂O₃ is mainly concentrated in the heavy minerals, (ii) those in which Fe₂O₃ is mainly concentrated in the coating materials, and (iii) those in which Fe₂O₃ is more or less equally concentrated in the heavy minerals and the coating materials.

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PURIFICATION OF SOME SAND DEPOSITS AROUND CAIRO FOR GLASS MAKING: PART II—METHODS OF PURIFICATION

M. M. MORSI*

Introduction

There are two aspects for the purification of sand¹: (i) the oversize and undersize material, which might lead to inhomogeneity in the glass melt must be removed; (ii) the impurities likely to impart undesirable colour to the glass must be removed or reduced.

Various investigators²⁻¹⁴ have studied the methods of treatment of sand for use in glass manufacture. These methods could be summarised as: (i) washing with water; (ii) separation of the heavy minerals using a magnet; shaking table or the froth flotation methods; (iii) removing the stained materials by using the attrition-scrubbing or the ultrasonic methods; (iv) the chemical treatment of the sand; and (v) combination of these methods.

Choice of the methods of purification

The process chosen for the purification of sand

depends on the manner in which the impurities are distributed¹⁵. Since iron is an impurity which needs to be considered, it is necessary to ascertain the forms in which it is present in the sand.

From previous studies¹⁶ it was found that iron is mainly concentrated in the fine particles especially those smaller than 0.1 mm and to a lesser extent in particles greater than 0.8 mm. The removal of these particle size fractions by washing with water and sieving should reduce largely the iron oxide content of the sand. In addition, the removal of these two fractions from the sand reduces the chances of inhomogeneity in the glass during the melting process¹. For further reduction of the iron, the subsequent treatment depends upon the type of the sand¹⁶.

Experimental

Samples collection and preparation are described elsewhere¹⁶. The silt-clay particles associated with the sand were removed by a washing process¹⁶. The process of washing was repeated

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until a suitable quantity (about 3 kg) of the washed and dried sand was obtained for each sand. Its iron content was determined (Table I). The washed and dried sand was then screened for 5 minutes over a sieve with 0.8 mm opening. The iron content of the fraction less than 0.8 mm was determined (Table I). The subsequent treatment of the three types of sand (Tables II to IV) was as follows:

Sand of type I (sample nos 1, 4b, 7b, 8 and 9a): The fraction of these sand (Table II) less than 0.8 mm in diameter was quartered and two representative portions were prepared. On each portion the process of heavy mineral separation was carried out by two different methods, *eg*, (i) froth flotation and (ii) magnetic separation.

TABLE I

Percentage of iron oxide in the sand after washing with water and then after screening on sieve with 0.8 mm opening

Locality	Sample number	Original Fe_2O_3 content	Iron remaining after	
			Washing	Sieving
Cairo-Suez Road	1	0.451	0.434	0.419
Almaza	2	0.476	0.371	0.324
Manshiat El-Bakri	3	0.315	0.222	0.185
El-Nahadein	4a	0.244	0.202	0.187
	4b	0.392	0.230	0.145
El-Nassr City 7th	5a	0.532	0.355	0.186
	5b	0.394	0.224	0.135
	5c	0.459	0.361	0.360
Liblaba	6	0.280	0.250	0.163
Maadi	7a	0.254	0.180	0.169
	7b	0.263	0.210	0.210
	7c	0.277	0.164	0.136
Helwan	8	0.902	0.735	0.712
Kafr El-Ilw	9a	0.442	0.283	0.210
	9b	0.493	0.445	0.402
El-Haram	10	0.899	0.765	0.512

TABLE II

Percentage of iron oxide in the sand of type I

Sample number	Original sand	Fraction less than 0.8 mm	Fe_2O_3 in the	
			Sand after purification by	
			Magnetic method	Flotation method
1	0.451	0.419	0.266	0.105
4b	0.392	0.145	0.081	0.113
7b	0.263	0.210	0.170	0.073
8	0.902	0.712	0.709	0.483
9a	0.442	0.210	0.169	0.160

The froth flotation was done by using a locally made laboratory Faggegrene type machine. A fixed speed for the impeller, 2000 rpm, was used during the experiment. The prepared samples were agitated at about 60 per cent solid for 3 minutes with sodium carbonate (0.7 to 0.8 kg/ton) and oleic acid (0.6 kg/ton)⁸. Then, the pulp was diluted to 20-25 per cent solid and the flotation was carried out for 5 minutes in this weak alkaline medium (pH 8.0-8.5)¹⁴. The foamed froth was removed and the remaining sand was washed on a sieve with 0.1 mm opening. It was then dried and its iron content was determined.

The magnetic separation was done by using a locally made laboratory Mortsall type separator, where the dried fraction (-0.8 mm) was fed at a rate of about 0.25 ton/hr on the drum which revolved with a speed of 5 rpm. The material was split into three parts, the non-magnetic (tailings), middling and magnetic portion. The iron content of the non-magnetic portion was then determined.

Sand of type II (sample nos 2, 3, 4a, 5a, 5b, 5c, 6, 7a, 7c, 9b, and 10): The sand fractions (Table III) less than 0.8 mm were agitated at about 60 per cent solid for 25 minutes. Pulp with percentage of solid more than 60 per cent used, was found to be ineffective due to the partial effect of the rotated impeller on the sand parti-

cles far from its vicinity. After agitation the sands were washed on sieve with 0.1 mm opening, dried and their iron content was determined (Table III).

TABLE III

Percentage of iron oxide in the sand of type II

Sample number	Fe ₂ O ₃ in the		
	Original sand	Fraction less than 0.8 mm	Sand after mechanical attrition
2	0.476	0.324	0.204
3	0.315	0.183	0.125
4a	0.244	0.187	0.116
5a	0.532	0.186	0.053
5b	0.394	0.135	0.058
5c	0.459	0.360	0.299
6	0.280	0.163	0.106
7a	0.254	0.169	0.128
7c	0.277	0.136	0.041
9b	0.493	0.402	0.350
10	0.899	0.512	0.330

TABLE IV

Percentage of iron oxide in the sand of type III

Sample number	Fe ₂ O ₃ in the		
	Original sand	Fraction less than 0.8 mm	Sand after treatment*
3	0.315	0.185	0.11
4a	0.244	0.115	0.07
5a	0.532	0.186	0.02
7a	0.254	0.169	0.06
7b	0.263	0.210	0.07

*Mechanical attrition followed by flotation process

Sand of type III (sample nos 3, 4b, 5a, 7a, and 7b): A suitable amount of the sand (Table IV) fractions less than 0.8 mm were subjected to a combination of the mechanical attrition and flotation processes after which the iron content of the resulting sand was determined.

The iron oxide was determined colorimetrically¹⁶.

Results and discussion

The results obtained after the different purification processes carried out on the three types of sand are given in Tables I to IV.

The washing process and the subsequent removal of the particles greater than 0.8 mm, decreased the iron content of the sand to a measurable extent. For example Fe₂O₃ of sand 4a was decreased from 0.244 to 0.187 per cent and of sand 8 from 0.902 to 0.712 per cent (Table I).

The original iron content of sand of type I was reduced to the range from 0.081 (sample no 4b; Table II) to 0.709 per cent (sample no 8; Table II) after being subjected to washing, screening and magnetic separation. The amount of iron oxide remaining after flotation varied from 0.073 per cent (sample no 7b; Table II) to 0.483 per cent (sample no 8; Table II). Thus it was evident that the flotation method was more effective than the magnetic method in lowering the amount of the iron oxide of most of the sand of type I (Table II). This may be attributed to: (a) not all the iron bearing minerals are strongly or moderately magnetic (as magnetite and ilmenite respectively) and hence, they are liable to be separated with the iron bearing minerals during the flotation process rather than by the magnetic process; (b) some of the quartz grains which are partially covered with dense coating material, may float as heavy mineral grains bearing iron oxide in their composition, since it is evident¹⁰ that particles can float even when their surfaces are not completely covered with collector.

Sand of type II (Table III) were found after mechanical attrition to contain iron oxide in amounts ranging between 0.041 per cent (sample

no 7c; Table III) and 0.350 per cent (sample no 9b; Table III).

Mechanical attrition followed by flotation process carried out on sand of type III produced sand with iron content varying from 0.02 (sample no 5a; Table IV) to 0.11 per cent (sample no 3; Table IV).

Conclusion

Sand from 10 localities around Cairo were investigated for beneficiation. The washing and screening processes decreased considerably the iron content of the sand, which became suitable for the manufacture of green and low grade colourless glass.

By the suitable purification methods the sand of (a) El-Nahadein, El-Nassr City 7th and Maadi became suitable for the manufacture of all types of commercial glasses including white colourless bottles and tableware, (b) sand from Cairo-Suez Road, Almaza, Manshiat El-Bakri, Liblaba and Kafr El-Ilw became suitable for the manufacture of lower grade colourless glass including

plate glass, and (c) sand from Helwan and El-Haram became suitable for the manufacture of coloured as well as sheet and plate glasses.

Summary

Suitable method for purification of sand from ten localities around Cairo consisted mainly of the removal of their silt-clay portion and the coarse grains (+0.8 mm) by simple washing and dry screening. Further reduction of the iron oxide content could be obtained by separation of their heavy minerals using flotation method rather than magnetic separation method or by separation of the coating materials using the mechanical attrition method or by mechanical attrition and flotation technique, according to the form in which iron oxide content was mainly present.

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A RAPID METHOD FOR THE DETERMINATION OF WATER CONTENT IN GLASS MIXES BY A WAVEGUIDE

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Introduction

Several methods can be used¹⁻⁶ for the measurement of the dielectric constant and loss in the microwave region. The method used in this work involved standing wave measurements in a rectangular waveguide⁵. It was simplified to allow rapid estimation of the water content in the glass mixes used in glass industry, to control the moisture content to the required percentage.

Theory

Let a part of the waveguide be filled with a material of dielectric constant ϵ^* as shown in Fig 1 and the waves propagating from the source be incident normally at the surface of the material. If the standing wave ratio measured in front of the air-dielectric boundary is σ , then the reflection coefficient R at the boundary of the dielectric is given by:

$$R = |R| e^{i\phi} = \frac{1-S}{1+S} e^{i\phi} = \frac{r-1}{r+1} \quad \dots \quad (1)$$

where ϕ is the phase change on reflection and r is the normalised input impedance at the boundary and S is equal to $1/\sigma$.

If the sample used is very lossy and of sufficient length and backed by a short circuiting plate, then the second reflection is negligible as seen from the input of the waveguide and R is still given by equation (1). But, for a low-loss dielectric, this effect must be taken into consideration since it influences R and, therefore, S will be affected.

In glass mixes which are not very lossy, it is better to interpose a quarter wavelength of air filled line between the back face of the test specimen and the terminating plate to eliminate the second reflection.

Knowing S and ϕ , r can be obtained using the Smith's chart⁷. The input impedance r changed with the change of the dielectric constant ϵ^* . The value of r thus obtained was plotted as a function of W , the water content of the mix. From the curve it was possible to deduce the water content in any given sample.

Experimental

The apparatus used^{7,8} is shown in Fig 2. The microwave generator working at a frequency of 8.630 GHz was followed by a variable attenuator, a slotted section with its probe and indicator, the test cell and a variable short. The cell consisted of a piece of waveguide 5.6 cm long and closed from both sides by thin mica windows. The same weight of glass mix was used for each measurement in order that the packing of the particles will be the same. The glass mix was dried completely before carrying out the first measurement having 0 per cent water content. Water was then added in steps of 0.5 gm water to 99.5 gm of dry sample, till a concentration of 5.5 gm water in

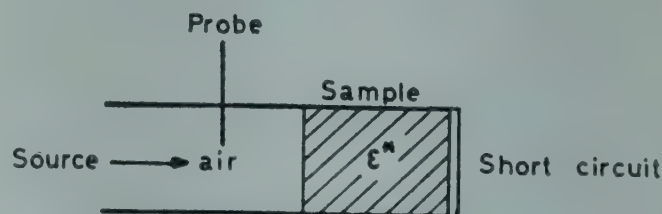


Fig 1
Waveguide filled with dielectric material (constant ϵ)

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94.5 gm of dry sample was reached and mixed very well before filling the cell. This range of water content is chosen because in industrial purposes a water content ranging between 4 to 5 per cent is needed. The standing wave ratio $1/S$ is obtained by measuring the difference Δx between the probe positions at which the power had twice its minimum value⁹ and substituting in the equation (2):

$$S = \frac{\pi \Delta x}{\lambda_g} \quad \dots (2)$$

also, from the position of the first minimum from the interface, ϕ can be computed. Using the Smith's chart, these readings were converted into the real (X) and imaginary (Y) parts of the input impedance r . The results obtained are given in Tables I and II. These experiments were repeated several times and they were reproducible to within 5 per cent. Log X versus

TABLE I

Results obtained for the different concentrations of water in the dry sample

Water content	Standing wave ratio (σ)	Shift of minimum (wave length)	Impedance (X+iY)	$2 + \log X$
0.0	52.0	0.025	0.020+i 0.16	0.30
0.5	52.0	0.012	0.020+i 0.08	0.30
1.0	43.0	0.012	0.023+i 0.08	0.36
1.5	28.9	0.016	0.040+i 0.10	0.60
2.0	19.1	0.017	0.050+i 0.11	0.70
2.5	19.0	0.026	0.055+i 0.16	0.74
3.0	11.5	0.020	0.090+i 0.12	0.95
3.5	8.0	0.009	0.125+i 0.06	1.10
4.0	8.7	0.021	0.120+i 0.13	1.08
4.5	7.8	0.019	0.135+i 0.12	1.13
5.0	4.8	0.040	0.220+i 0.24	1.34
5.5	3.4	0.046	0.320+i 0.27	1.51

TABLE II

Results obtained for Δx at the different water concentrations. Δx is defined in equation (2)

Water content	Δx	$2 + \log \Delta x$
0.0	0.03	0.5185
0.5	0.03	0.5185
1.0	0.04	0.6021
1.5	0.06	0.7782
2.0	0.09	0.9542
2.5	0.09	0.9542
3.0	0.15	1.1761
3.5	0.20	1.3010
4.0	0.20	1.3010
4.5	0.22	1.3424
5.0	0.44	1.6435
5.5	0.59	1.7709

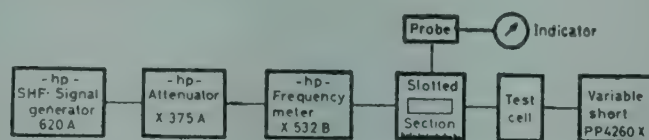


Fig 2
Block diagram of the apparatus used

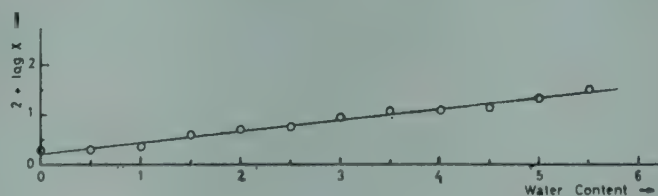


Fig 3
Relation between the input impedance and the water content

the percentage of water in the glass mix is plotted in Fig 3. A straight line curve was obtained from which any unknown water concentration could be deduced. The measurement and calculation for each unknown sample took about ten minutes. It is recommended

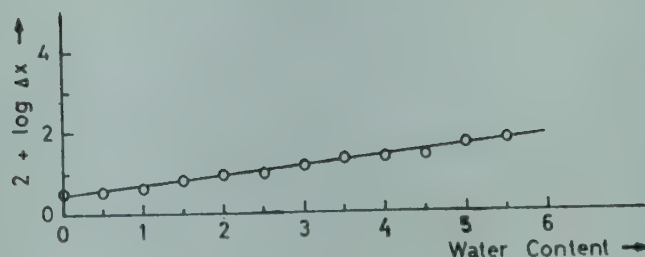


Fig 4

Relation between Δx and water content, where Δx is proportional to the standing wave ratio

to empty the cell, fill it again with the sample and repeat the measurement to be sure that the results are reproducible because sometimes the mix is collected in small lumps due to the presence of water and these give incorrect results.

To find the result more rapidly, $\log \Delta x$ versus water content is plotted in Fig 4. A

straight line curve was obtained which could equally be used as in Fig 3 to find out any unknown water concentration. This spares the time of measuring and computing ϕ and r . In this case the measurement will take only about five minutes. The method is a practical one for measuring the water content in the glass mix.

Summary

A rapid method which allows the estimation of the water content in glass mixes in a few minutes is described. It involves the measurement of the input impedance at the air-dielectric boundary in a waveguide. The apparatus is calibrated using dry samples and samples having known percentage of water, the calibration curve is used to estimate unknown percentage of water in other samples to an accuracy of better than 5 per cent.

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HIGH TEMPERATURE STABLE CERAMIC STAINS: ZIRCON-PRASEODYMIUM YELLOW AND ZIRCON-VANADIUM BLUE

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Introduction

During the last two decades the need for stability of ceramic colours with improved control of shade at high temperature firing conditions particularly in the sanitary and wall tiles field has intensified research and development work on colouring oxides or stains based on zirconium silicate.

F. T. Booth and G. N. Peel¹ concluded that zircon itself did not yield the desired colour and it was essential to use zirconia and silica to form zircon. The development of colours was explained on the basis of latching of some colourant ions like vanadium, praseodymium, *etc*, in the zircon lattice during combination of zirconia and silica to form zircon.

The work for developing high temperature stable ceramic stains from indigenously available zirconia and praseodymium oxide was taken up at the Institute, with an aim to achieve self reliance.

Literature on the mechanism of colour formation

Zr-V blue: Recent studies^{1,7} on the mechanism of formation of zircon stains have established that zircon-vanadium blue stain is a solid solution formed as a result of the tetravalent vanadium colouring ion entering the zirconium silicate (ZrSiO_4) lattice at the time of its formation by the reaction between zirconia (ZrO_2) and silica (SiO_2).

Presence of zirconia in the form of zircon in the blue stain has been confirmed by X-ray investigation^{1,4}. The formation of blue stain depends entirely on the reaction between

zirconia and silica as separate components and the colour could not be produced from zirconium silicate itself.

Based on dta studies on the formation of zircon in the $\text{ZrO}_2\text{-SiO}_2\text{-V}_2\text{O}_5$ system where no alkali or fluorine was present, V.I. Matkovich and P. M. Corbett³ have suggested a mechanism involving reaction of zirconia first with vanadium pentoxide at about 730° forming $\text{ZrO}_2 \cdot n\text{V}_2\text{O}_x$, where x is either 4 or 5. This reaction product then readily reacts with silica to form zircon yielding a light blue colour. The light blue colour was attributed to the presence of a small percentage of tetravalent vanadium ion in solid solution in zircon on the analogy of the usual blue colour of salts containing this ion. The reduction of vanadium from pentavalent to tetravalent state was also explained on the possibility of a reaction between zirconia and vanadium tetroxide, since at high temperature vanadium pentoxide loses oxygen to form mixtures of lower oxides. Recently, T. Demiray, *et al*⁴, have also shown that Zr-V blue colour could not be developed in hydrogen where the trivalent vanadium ion would be its most stable valency state and have established that tetravalent vanadium is solely responsible for the blue colour of the stain in which some V^{4+} ions replace some Zr^{4+} ions in the zircon lattice.

The addition of sodium fluoride is stated to be essential in the development of intense blue colour in the Zr-V stain and 80 per cent conversion to zircon was reported when the $\text{ZrO}_2\text{-SiO}_2\text{-V}_2\text{O}_5\text{-NaF}$ system stain batch was calcined¹ for one hour at 950° . A number of investigations for elucidating the role of sodium fluoride in the formation of zircon at these low temperatures have been reported⁵, but the precise

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function of the fluoride has not yet been fully understood. A partial explanation has been found in the work of R. A. Eppler^{6(a)} who applied the well-known 'marker-technique' for solid state reaction to the $\text{ZrO}_2\text{-SiO}_2\text{-V}_2\text{O}_5\text{-NaF}$ system. The results indicate that the fluoride acts mainly as a transporting agent involving reaction between SiO_2 and NaF to form volatile SiF_4 which carries the Si^{4+} to the ZrO_2 sites facilitating formation of zircon. It has also been demonstrated that Si^{4+} is the only mobile cation which moves to zirconia layer and not vice-versa and vanadium being volatile is also transported to the zirconia layer together with SiF_4 .

Zr-Pr yellow: The reactions involving formation of Zr-Pr yellow stain have also been shown to be analogous to those involved in the Zr-V blue stain, the formation being possible only when zirconia and silica react as separate components to form zirconium silicate in the presence of praseodymium oxide and sodium fluoride¹. X-ray investigations⁷ have also shown that zirconia is present in the stain as zircon containing some Pr^{4+} in the lattice taking the place of some Zr^{4+} ions.

R. A. Eppler^{6(b)} by applying the 'marker-technique' for solid state reaction to the $\text{ZrO}_2\text{-SiO}_2\text{-Pr}_6\text{O}_{11}\text{-NaF}$ system, has also shown

that in addition to the reaction of SiO_2 with NaF with the formation of volatile SiF_4 in this system, praseodymium oxide, too, reacts with the fluoride and is transported to the reaction sites in the vapour state.

Experimental

Raw materials: The raw materials used were ammonium metavanadate (98 per cent) and indigenously available zirconia (99.5 per cent ZrO_2), praseodymium oxide (99 per cent Pr_6O_{11}), sodium fluoride (95 per cent) and quartz powder (99 per cent SiO_2). It was found advantageous to use silica in its more reactive form of silica sol, which was prepared by neutralising a dilute solution of sodium silicate with hydrochloric acid⁸. The precipitate obtained was washed thoroughly with over flowing tap water to remove the sodium chloride followed by pressing in markin cloth to drain out water and then drying slowly at 60-70° in an oven.

Procedure for preparation of the stain: The mixing of the stain batch was carried out by wet grinding in porcelain milling jar. The milled bsatch was then calcined in refractory crucibles in electrically heated muffle furnace with optimum time-temperature schedule for each stain. After calcination, the stains formed a lumpy mass which was very hard particularly in case of Zr-Pr yellow stain. The lump was ground in stainless steel mortar to pass through 100 mesh BS sieve. Finally the ground stain was washed with hot water and then made fine by wet milling followed by drying before storing.

Glazes: Three types of fritted borosilicate glazes (lead-free transparent, lead-free zircon opacified and lead-bearing zircon opacified) which are commonly used in sanitaryware and pottery industries, were used in evaluating the intensity and colouring shade obtained from the stains. The glaze compositions are shown in Table I. The stains were wet milled with the glaze together with clay (10 per cent) and zircon opacifier (2-3 per cent) as mill additions. For application of the glazes, unglazed sample tiles

TABLE I

Molecular formulae of fritted glazes

Constituents	Glaze G-1 (lead-free transparent)	Glaze G-2 (lead-free opaque)	Glaze G-3 (lead-bear- ing opaque)
SiO_2	3.50	3.48	3.13
ZrO_2	—	0.14	0.26
Al_2O_3	0.35	0.35	0.37
B_2O_3	0.60	0.60	0.38
PbO	—	—	0.02
ZnO	0.30	0.30	0.25
BaO	—	—	0.06
CaO	0.40	0.40	0.23
MgO	—	—	0.17
KNaO	0.30	0.30	0.27
Glost firing at (°C)	1050-1100	1050-1100	1050-1100

TABLE II

Zircon-praseodymium yellow stains

Constituents	Stain numbers														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
ZrO ₂	61.5	61.5	61.5	61.5	61.5	18.0	45.8	73.6		61.5	61.5	61.5	61.5	61.5	61.5
SiO ₂ (-200 mesh)	30.1	30.1	30.1	30.1	30.1	73.6	45.8	18.0		30.1	30.1	30.1	30.1	30.1	30.1
Pr ₆ O ₁₁ (99.9%)		4.9	6.0												
Pr ₆ O ₁₁ (99%)	4.9			3.0		4.9	4.9	4.9	5.0	4.9	4.9	4.9	4.9	4.9	4.9
Pr ₆ O ₁₁ (90%)					6.7										
NaF	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5		2.0	5.0
Al ₂ O ₃										4.0	4.0				
TiO ₂										4.0		4.0			
ZrSiO ₄									91.5						
Colour (yellow) intensity of stain	S	S	S	M	M	VL	L	L	PC	M	M	M	PC	M	S

S—strong; M—medium; L—light; VL—very light; PC—pale creamish

were used and the coated tiles were fired in electrically heated muffle furnace over a three-hour cycle with soaking for one hour at glost firing temperatures of 1100-1150°.

Results and discussion

Zircon-praseodymium yellow: Zircon-praseodymium yellow stains were prepared by calcining an equimolar mixture of zirconia (ZrO₂) and silica (SiO₂) with praseodymium oxide (Pr₆O₁₁) and sodium fluoride (NaF) at temperatures of about 1250° in an oxidising atmosphere. The compositions of Zr-Pr yellow stains are shown in Table II. In addition to the chemical composition of the stain, the intensity of the yellow colour was observed to depend greatly on the calcination schedule and temperatures. The mass after calcining at 1250° turned to a hard lump and only marginal improvement in colour intensity was observed when the hard lump obtained after calcining at 1250° was ground fine and recalcined at 1250°.

Table II shows that the proportion of Pr₆O₁₁ required to yield the maximum intensity in the yellow stain corresponded to about 5 per cent, the intensity remaining unchanged with any further increase in Pr₆O₁₁. The stain 1 (Table II) was prepared with the use of Pr₆O₁₁ (4.9 per cent) of 99 per cent purity and an intense yellow colour was produced. No further improvement in colour intensity was obtained when Pr₆O₁₁ (4.9 per cent) of a higher purity (99.9 per cent) was used as in the stain 2 or when the amount of even the high purity Pr₆O₁₁ was increased to 6 per cent as in the stain 3. This indicates that a limited quantity of Pr₆O₁₁ was responsible in the formation of yellow colour, thus limiting the intensity of the stain. It was also noticeable that a reduction of the content of Pr₆O₁₁ from 4.9 per cent to 3 per cent as in the stain 4 caused a decrease in the colour intensity. The colour intensity of the stains (1, 2 and 3) as well as their colouring effect in the glazes (Table I) are similar. Maximum economy is effected by using

Pr_6O_{11} of purity 99 per cent for the manufacture of Zr-Pr yellows.

Pr_6O_{11} of purity 90 per cent was also tried in the preparation of the Zr-Pr yellow stains. It was observed that the use of lower purity (90 per cent) Pr_6O_{11} with an amount up to 6.7 per cent as in the stain 5, did not yield a colour intensity equal to that of stain 1 (using 4.9 per cent of Pr_6O_{11} of 99 per cent purity). This may be attributed to the presence of other impurities in the lower purity oxide.

The presence of equimolar quantities of ZrO_2 and SiO_2 in Zr-Pr stains showed that the colour intensity was maximum whereas, the presence of ZrO_2 and SiO_2 (stains 6, 7 and 8; Table II) in varying molar proportions showed that the colour intensity was noticeably reduced irrespective of the direction in which the $\text{ZrO}_2/\text{SiO}_2$ molar ratio was varied from the equimolar ratio.

The fineness of ZrO_2 and SiO_2 was observed to have an important effect on the colour intensity of the stains. The fineness of ZrO_2 used in the preparation of the stains was —300 mesh BS sieve. The colour of the stain using quartz powder of fineness—300 mesh BS sieve was noticeably more intense than that of the stain 1 using quartz powder of fineness—200 mesh BS sieve. A similar increase in colour intensity was obtained using silica sol in place of quartz powder of fineness —200 mesh BS sieve.

An effort to produce Zr-Pr yellow stain by replacing ZrO_2 and SiO_2 with the cheaper zircon sand (ZrSiO_4) as in stain 9 only produced a pale creamish colour without any colouring effect in the glazes (Table I). Al_2O_3 and TiO_2 together (as in the stain 10) or separately (as in the stains 11 and 12) was observed to reduce the colour intensity. Addition of Al_2O_3 or TiO_2 separately was observed to weaken the colour.

The addition of NaF as a mineraliser was observed to be essential in the development of Zr-Pr yellow colour. The stain 13 using no NaF produced only a pale creamish colour without producing any colouring effect in any of the glazes (Table I). The stain 14 containing 2

per cent NaF produced a light yellow colour. The intensity of the yellow colour appeared to be maximum with 3.5 per cent of NaF and further increase up to 5 per cent as in the stain 15 could not increase the colour intensity, but the hardness of the calcined mass was increased with increasing amounts of sodium fluoride.

Zr-Pr yellow stain had an intense lemon yellow colour and its colouring effect in glazes was much cleaner and brighter in tone than that obtained from either zirconium-vanadium or tin-vanadium yellows⁹. Zr-Pr yellow had the advantage that it was not very sensitive to glazes and could be used over a range of glaze compositions with no appreciable change in intensity or shade. It was normally used in conjunction with 2-3 per cent zircon as mill added opacifier to obtain the satisfactory stabilising effect, the amount of opacifier depending upon the degree of opacity required. Zr-Pr yellow stains were tried in the glazes as shown in Table I. The transparent glaze (G-1) without any mill added zircon opacifier although produced a tone of yellow colour with the use of high content of the stain (10 per cent) but due to lack of opacity, the colouring shade was not uniform.

Lead free opaque glaze (G-2) produced the maximum colour intensity while the lead-bearing opaque glaze (G-3) appeared to reduce it slightly, particularly when a low content of the stain (1-2 per cent) was used. However, no difference in colour intensity or shade was observed between the lead-free or lead-bearing opaque glazes when the stain addition was increased to 3 per cent or more. Zr-Pr yellow stains can be used over a range of about 1 to 7 per cent in the glazes. Below 1 per cent an extremely weak colour was obtained and light to medium yellows were produced by the addition of 1-4 per cent of the stain. An intense lemon yellow colour was produced with 5 per cent of the stain, the intensity being only marginally increased up to 7 per cent but there was no noticeable increase in intensity with the stain above 7 per cent. Overgrinding of the glaze

with the stain also resulted in weakening the colour intensity.

The Zr-Pr yellow showed intense colour with firing of the glazes at 1050-1100° and only a marginal fading of colour was observed with increased firing temperatures. Such fading of colour could be minimised by increasing the content of the stain by 1-2 per cent even in the unfritted glazes with firing temperatures of 1300°. The Zr-Pr yellow also showed good colour intensity as body stain and also as under-glaze ceramic colour. The stain (5 per cent) also produced an intense lemon yellow colour in transparent enamels for sheet iron with firing temperatures of 800-820°

Zircon-vanadium blue: Zircon-vanadium blue was prepared by calcining an intimate mixture of zirconia (ZrO_2) and silica (SiO_2) in equimolar proportions in the presence of ammonium metavanadate (NH_4VO_3) and sodium fluoride (NaF) at temperatures of about 1000° in an oxidising atmosphere. Vanadium pentoxide (V_2O_5) can also be used in place of NH_4VO_3 but since better dispersion in intimate

mixing is obtained with the soluble salt, it is preferable to use NH_4VO_3 . The compositions of Zr-V blue stains are shown in Table III. For the formation of blue colour in this system the firing schedule and calcination temperature conditions had to be controlled within critical limits. Recalcination or rise of calcination temperatures did not show any improvement in the colour intensity.

Table III shows that the colour of the stains 1, 2 and 3 changed from yellow to bluish with increasing amounts of NH_4VO_3 and the stain 3 containing NH_4VO_3 (4 per cent) showed a strong blue colour. Further increase of the vanadate to 5 per cent and even to 7 per cent as in the stains 4 and 5 did not show any increase in the colour intensity. This indicates that only a limited amount of vanadium takes part in the formation of blue colour, thus limiting the intensity of the stain.

Like Zr-Pr yellows, it was observed that the colour intensity of the Zr-V blue stains was maximum with equimolar quantities of ZrO_2 and SiO_2 . The stains 6, 7 and 8 (Table III)

TABLE III
Zircon-vanadium blue stains

Constituents	Stain number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
ZrO_2	61.5	61.5	61.5	61.5	61.5	76.0	18.0	46.0		61.5	61.5	61.5	61.5	61.5	61.5
SiO_2 (-200 mesh)	30.1	30.1	30.1	30.1	30.1	16.0	74.0	46.0				30.1	30.1	30.1	30.1
SiO_2 (-300 mesh)										30.1					
Silica sol (dry)											40.0				
NH_4VO_3	2.0	3.0	4.0	5.0	7.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
NaF	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0		2.5	5.0	7.0
$ZrSiO_4$										91.5					
Colour intensity of stain	LY	BY	S	S	S	LG	LB	MB	Br	S	S	LY	LY	S	S

LY—light yellow; BY—bluish yellow; S—strong blue; LG—light green; LB—light blue; MB—medium blue; Br—brownish

were prepared with varying molar proportions of ZrO_2 and SiO_2 . It was observed that low contents of silica (stain 6) produced a greenish yellow colour and higher contents of silica (stain 7) produced a light blue colour. The intensity of blue colour of the stain 8, where the difference in molar proportions of SiO_2 and ZrO_2 was relatively less, was more intense than that of stain 6 and the colour intensity reached a maximum when equimolar quantities of ZrO_2 and SiO_2 were used as in the stain 3. The Zr-V blue stains could not be prepared from zirconium silicate (ZrSiO_4) itself but only from a combined reaction between ZrO_2 and SiO_2 when used as separate component. The stain 9 using ZrSiO_4 produced only a brownish colour.

The fineness of zirconia and silica used in the preparation of Zr-V blue stains was —300 mesh and —200 mesh BS sieve respectively. Use of more finer quartz powder (—300 mesh BS sieve, stain 10) or use of silica sol (stain 11) did not show any noticeable increase in the intensity of the blue colour (Table III).

Table III shows that the addition of NaF was essential in the development of blue colour. The intensity of the blue colour was observed to be maximum with 4 per cent of NaF as in the stain 3 and further increase to 5 per cent or even to 7 per cent (as in the stains 14 and 15) could not further improve the intensity of the blue colour. The stain 12 which did not contain sodium fluoride produced only a light yellow colour and the stain 13 containing low amounts of NaF (2.5 per cent) produced a pale yellow colour with a bluish green tinge.

Zr-V blue had a good turquoise blue colour and could be used as a glaze and underglaze colourant. Development of Zr-V blue stains reduced the demand for cobalt blue stains but they are not so intense as those obtained from cobalt blue stains which have a reddish tone, whereas, Zr-V blue stains have a greenish tone¹⁰. Like Zr-Pr yellow stain, Zr-V blue can also be used over a range of glaze compositions but it is preferable to use zircon opacifier (2-3 per cent) with the stain, as this prevents solubility

of the colour in the glaze and consequent loss of intensity. The Zr-V blue stains were tried in the glazes shown in Table I. The transparent glaze (G-1) without any mill added zircon opacifier produced a pale bluish colour with uneven colour tone.

It was also observed that the lead-free opaque glaze (G-2) produced the most intense colour but the lead-bearing opaque glaze (G-3) although increased the brilliance but appeared to decrease the colour intensity slightly. About 1-7 per cent of the Zr-V blue stain can be added to the glaze, less than this produced a very weak tint and more than this did not show any increased intensity. A strong turquoise blue was obtained with the addition of 5 per cent of the stain.

Zr-V blue stains can be used with glazes over a wide firing range and with increasing firing temperatures above 1100° only a marginal fading of colour was observed. Such fading of colour could be overcome by increasing the content of the stain by 1-2 per cent. A good colour was also obtained with the stain (5 per cent) when used in transparent enamels for sheet iron at firing temperatures of $800-820^\circ$.

Summary

The Zr-Pr yellow and Zr-V blue stains could not be prepared from zirconium silicate (ZrSiO_4) but only from ZrO_2 and SiO_2 as separate components. The colour was developed only when the colourant ions (*viz.* Pr and V) enter the ZrSiO_4 lattice at the time of its formation.

The intensity of both the stains largely depended on the proportions of ZrO_2 and SiO_2 . The maximum intensity was obtained with equimolar quantity of ZrO_2 and SiO_2 .

The intensity of both the Zr-Pr yellow and Zr-V blue gradually reached a maximum limit with increase in NH_4VO_3 up to 4 per cent for the blue and of Pr_6O_{11} up to 5 per cent for the yellow stains. Further increase in V_2O_5 and Pr_6O_{11} did not increase the intensity any further.

Addition of NaF was essential in the forma-

tion of colour in both the stains. The colour intensity was maximum with the addition of 3.5 per cent for the Zr-Pr yellow and 4 per cent for the Zr-V blue stains. Further increase in NaF additions did not lead to any increase in the colour intensity in either of the stains.

The intensity of colours of both the stains greatly depended on the calcination schedule and temperatures.

The stains worked best in zircon opacified glazes and the addition of 2-3 per cent of zircon

opacifier with the stain was preferable to stabilise the colouring shade.

The stains could be used in the glaze with amounts of 1-7 per cent, less than this produces a very weak tint and more than this has no advantageous effect on the colour intensity.

Acknowledgment

The authors thank Shri K. D. Sharma, Director of the Institute, for his kind permission to publish this paper.

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(Ms received November 2, 1976)

CGCRI CELEBRATES SILVER JUBILEE

The Central Glass and Ceramic Research Institute celebrated its Silver Jubilee on March 12, 1976. The Indian Ceramic Society held its 40th Annual Session during the celebrations. The function was inaugurated by Shri Siddhartha Shankar Ray, Chief Minister, West Bengal. Shri Sankar Ghosh, Minister for Finance, Planning and Development, West Bengal, was the Chief Guest. Dr Zainal Abedin, Minister for Small Scale Industries, West Bengal and Prof Y. Nayudamma, Director General, Scientific and Industrial Research, graced the function by their presence. Prof J. White, Dyson Professor of Refractories, Sheffield University, UK,



Fig 1

Shri Siddhartha Shankar Ray, Chief Minister of West Bengal, delivering the inaugural address. Sitting on his right is Prof Y. Nayudamma, Director General, Scientific and Industrial Research



Fig 2

Prof Y. Nayudamma, Director General, Scientific and Industrial Research, delivering his address. Sitting on his left is Shri Siddhartha Shankar Ray, Chief Minister of West Bengal and on his right is Dr Zainal Abedin, Minister for Small Scale Industries, West Bengal

attended the function as a special guest. He delivered the Silver Jubilee Lecture on 'Phases and interfaces in ceramics'.

The Prime Minister, the President of CSIR, Shrimati Indira Gandhi, in her message of felicitations to the Institute stated "Glass has a multitude of uses ranging from the kitchen to the most sophisticated of scientific instruments. Deeper know-how of glass and ceramic technology is indispensable for progress. The career of the Central Glass and Ceramic Research Institute in Calcutta has been useful. The Institute has several achievements to its credit, especially the development of optical glass and of laser glass. The Institute's work has saved us resources which would have otherwise gone into imports. My good wishes for the Silver Jubilee

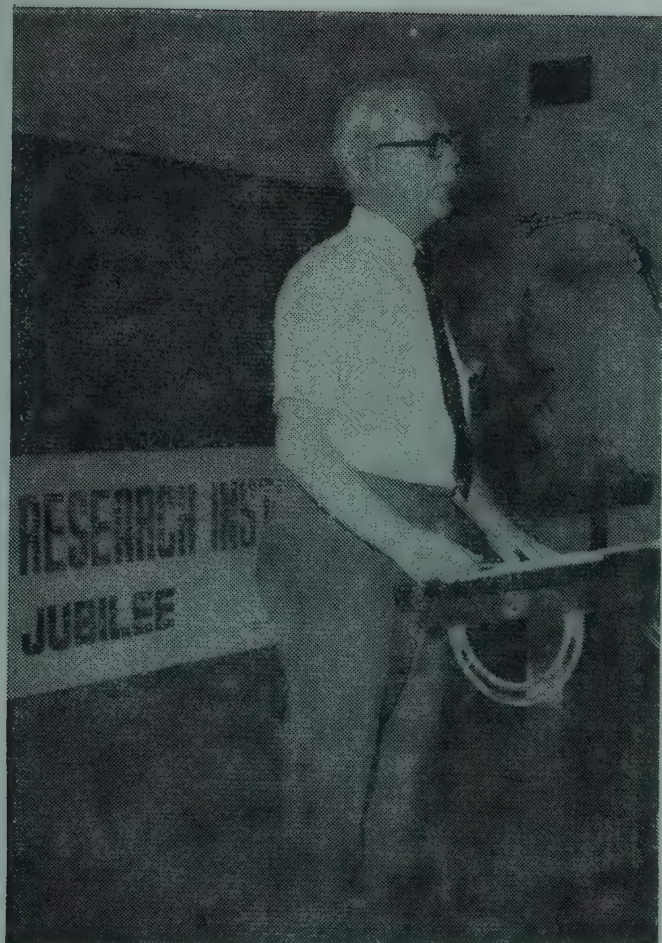


Fig 3

Prof James White, formerly Dyson Professor of Refractories, University of Sheffield, UK, delivering the Silver Jubilee commemoration lecture

celebrations of the Central Glass and Ceramic Research Institute”.

Inaugurating the Silver Jubilee celebrations, Shri Siddhartha Shankar Ray pointed out the remarkable progress made by the Institute, especially in the field of import substitution and utilisation of the country's raw material resources. He referred to the communication gap that kept the common people not adequately informed about the Institute's role in the economic and industrial advancement of the country. Science and technology should be geared to the benefit of the common masses. For establishing better communication with the entrepreneurs in the glass and ceramic field, the State Govt had established the West Bengal Ceramic Development Corporation which, he

hoped, would take advantage of the work done by the Institute. He also appreciated the sense of dedication and discipline among the workers of the Institute and said that no indiscipline would be tolerated here or anywhere else in the State. Shri Sankar Ghosh laid stress on the importance of import substitution and development of low-cost technology appropriate to the Indian conditions. He urged upon the scientists to undertake need based research and development work for the country's development, especially in the small scale sector requiring low-cost technology.

Dr Zainal Abedin referred to the inadequate attention the glass and ceramic industry of the



Fig 4

Shri Siddhartha Shankar Ray, Chief Minister, Shri Sankar Ghosh, Minister for Finance, Planning and Development and Dr Zainal Abedin, Minister for Small Scale Industries, West Bengal, at the exhibition. Shri K. D. Sharma, Director, CGCRI (back to the camera) explaining the exhibits. Prof Y. Nayudamma, Director General, Scientific and Industrial Research is at the rear (extreme right)

State received so far in spite of the State being rich in related raw materials. He hoped that the newly founded West Bengal Ceramic Development Corporation would catalyse the growth of the industry in the State.

Prof Y. Nayudamma, DGSIR, congratulated the Institute on its performance and paid glowing tribute to the foresight of Pandit Jawaharlal Nehru for ushering in an era of scientific and technological advancement in the country. He referred to the *Nehru-Bhatnagar effect* which sparked off a chain of National Laboratories in various disciplines in the country. He declared that a political will coupled with a clear scientific commitment formed the basis on which a nation built itself. The scientists and technologists should utilise the technological advances to meet the need of the weaker sections of the society.

Shri K.D. Sharma, Director, CGCRI, gave an account of the achievements of the Institute in the last 25 years in the various domains of glass and ceramics, particularly to meet the National needs in the field of the defence pro-

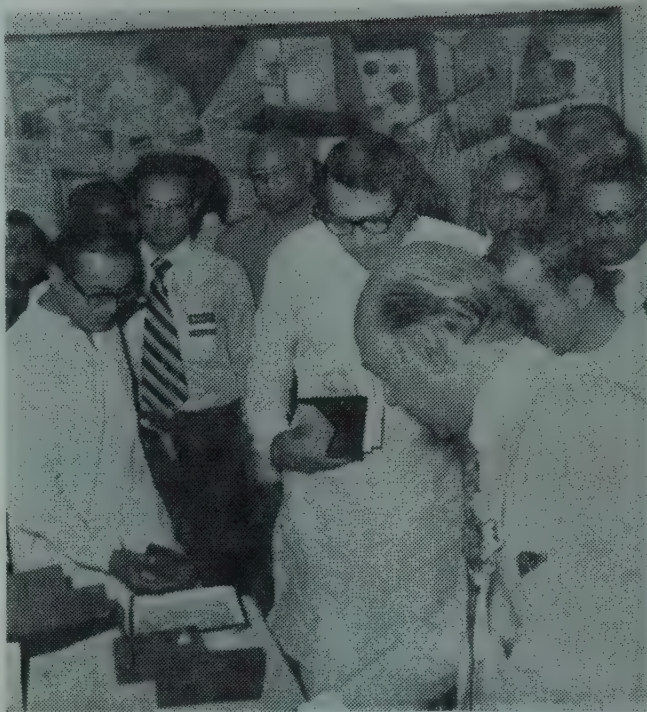


Fig 5

Shri K. D. Sharma, Director, CGCRI (extreme right foreground) explaining the process for foam glass developed at CGCRI to Shri Siddhartha Shankar Ray, Chief Minister (centre) and Shri Sankar Ghosh, Minister for Finance, Planning and Development, West Bengal (extreme left with foam glass in hand)



Fig 6

A view of the audience at the inauguration

duction and import substitution. He made particular reference to the self-reliance attained in the field of special glasses. The Institute had so far produced and supplied optical glass and special glass and ceramic articles worth over rupees one crore to defence and civilian consumers. The process for production of optical glass was leased out to Bharat Ophthalmic Glass Ltd, a Govt of India undertaking. This has made the country self-sufficient in this strategic material. Shri Sharma also referred to development of insulating bricks from waste mica the total production of which had exceeded Rs 2 crores, synthetic quartz single crystals required by the electronics industry, water filter candles for obtaining bacteria-free drinking water and laser glasses (neodymium-doped) for making range finders for defence use.

The President of the Indian Ceramic Society, Shri B. N. Bhaskar praised the contributions of the Institute. He emphasised upon the need for providing quality products to consumers at reasonable prices. He urged upon the Institute to put in extra efforts to assess the requirements of the industry and provide them with suitable technology.

Sardar Kishen Singh, Shri M. K. Ganpule and Dr H. K. Mitra, in their speeches complimented the Institute on its very useful contri-

butions during the last 25 years in the fields of glass, ceramics, refractories, mica, vitreous enamels, ceramic colouring materials, *etc*, in the twin spheres of advancement of knowledge as well as of applications in industry and defence.

At the end of the function Shri S. S. Verma, Chairman of the Silver Jubilee Reception Committee proposed a hearty vote of thanks to all concerned. Referring to the learned and appreciative speeches of the distinguished industrialists and technologists, Shri Verma assured them that the scientists of the Institute will continue to give their best efforts for assisting the industry in the dedicated spirit propounded by Prof Nayudamma, DGSIR, whom he thanked for giving a bold lead to the scientists of the National Laboratories.

Thirtynine staff members who completed 25 years of service were awarded commemorative silver medals. A special medal was awarded to Dr Atma Ram, the retired founder-director of the Institute, an ex-DGSIR, for his outstanding services towards establishment and growth of the Institute.

The CGCRI was declared open by late Dr B. C. Roy on August 26, 1950. A history of the Institute has been published in this journal Vol 22, No 4 (1975), pp 208-217 and Vol 23, No 2 (1976), pp 72-85.

BOOK REVIEW

An introduction to the principles of surface chemistry. R. Aveyard and D. A. Haydon, Cambridge University Press, Bentley House, 200 Euston Road, London NW1 2DB, page 232, price £2.40.

Surfaces and interfaces play an important role in biology as well as in organic and inorganic process technology. The importance of this subject is being increasingly felt in the field of materials science. After the availability of new tools like ESCA, Auger electron spectroscopy, *etc*, a tremendous interest has been created in understanding the nature and chemistry of solid surfaces. A series of books dealing with chemistry of surfaces and in thin films or surfaces, which

are of great interest to materials scientists have recently appeared. This book is an important addition to text books dealing with chemistry of surfaces. It deals both with liquid and solid surfaces and its treatment is in most cases quantitative. The chapter on solid-gas interface (Chapter 5) may prove particularly valuable to the materials scientists.

The chapters have been divided as follows: (i) Some general principles relating to surfaces; (ii) Electrical potentials at interfaces; (iii) Liquid interfaces; (iv) Polarised and non-polarised electrode surfaces; (v) The solid-gas interface; (vi) The solid-liquid interface.

—J. Mukherji

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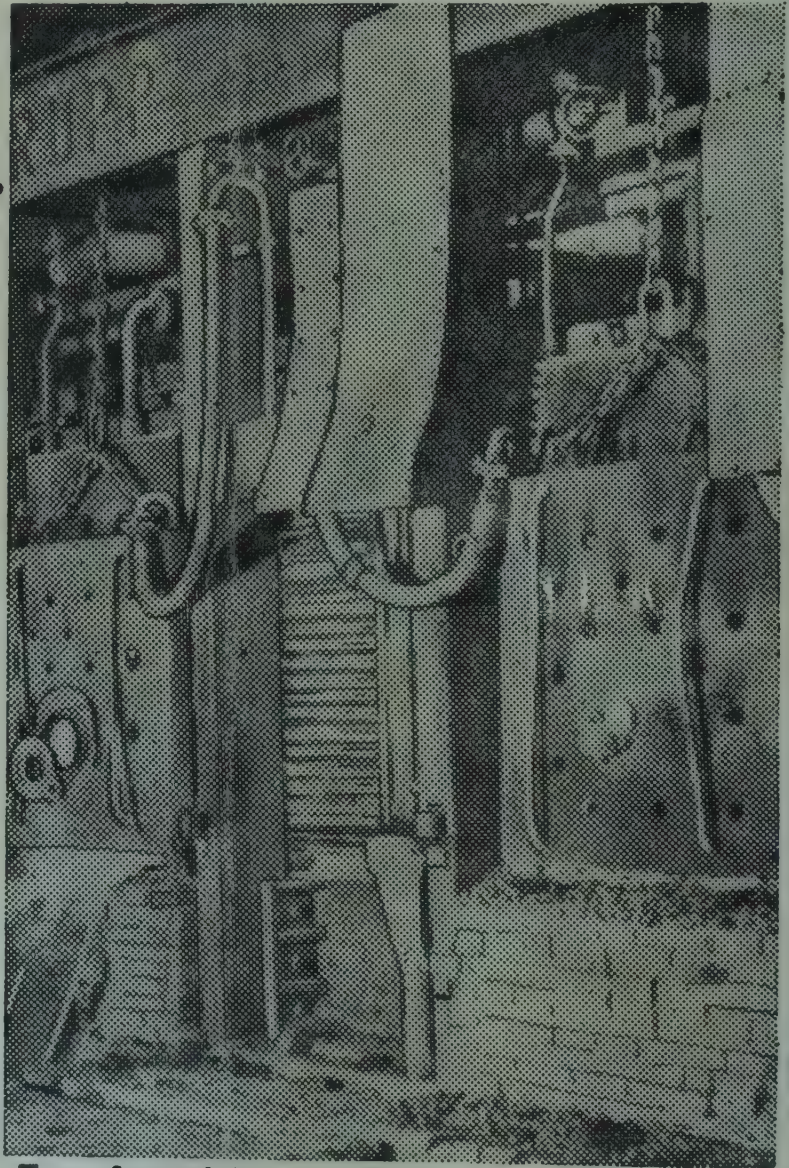
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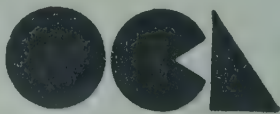
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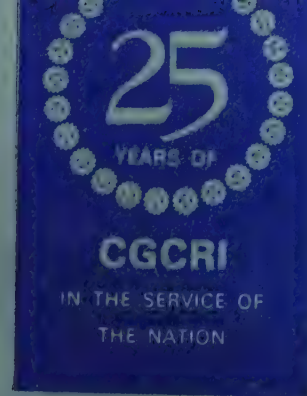
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Studies on high temperature ceramic coatings.

N. Roy and S. S. Verma, *Cent Glass Ceram Res Inst Bull*, 23 (4) 125-132 (1976).

The compositions and techniques of application of high temperature ceramic coatings used on nimonic alloy and heat resistant steel components of jet aero-engines' exhaust system are presented.

Effect of processing variables on the properties of high alumina ceramics.

S. Chatterjee, S. K. Guha, B. K. Sen and Sudhir Sen, *Cent Glass Ceram Res Inst Bull*, 23 (4) 132-136 (1976).

Process variables like the grinding period, the size, shape and quality of grinding media; the type and nature of grinding equipment were studied in relation to their effect on the properties of high alumina ceramic compositions.

Reduction in the Na_2O content resulted not only in improved electrical properties but also contributed largely to a significant reduction in the sintering temperature.

The effect of RO , R_2O_3 and RO_2 additions on MnO_2 -containing $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glasses.

H. A. El-Batal and N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, 23 (4) 136-143 (1976).

Optical absorption and magnetic susceptibility of manganese dioxide containing soda borate glasses were determined. In the base glass B_2O_3 80, Na_2O 20 wt per cent, Na_2O was replaced by 1, 5 and 10 parts of MgO , ZnO , CaO , SrO , BaO or CdO and B_2O_3 by 2, 5, 10 and 15 parts of Al_2O_3 or SiO_2 .

Infrared studies of some Jammu clays.

S. N. Khosla, C. S. Gupta and R. K. Bedi, *Cent Glass Ceram Res Inst Bull*, 23 (4) 144-149 (1976).

Infrared studies of six clays from Jammu region were carried out to identify the mineral constituents. One of the clays had montmorillonite. The second was a mixture of kaolinite, illite and quartz. Rest of the clays contained montmorillonite associated with illite in different proportions.

A low solubility lead-boracic glaze: Part II.

R. V. Lele and R. N. Ray, *Cent Glass Ceram Res Inst Bull*, 23 (4) 149-152 (1976).

A transparent glaze having the molecular composition 0.110 K_2O , 0.086 Na_2O , 0.532 CaO , 0.106 BaO , 0.165 PbO , 0.286 Al_2O_3 , 3.300 SiO_2 and 0.386 B_2O_3 is developed. The glaze has a wide firing range and good crazing and scratch resistance.

Etudes sur les revêtements céramiques pour haute température.

N. Roy et S. S. Verma, *Cent Glass Ceram Res Inst Bull*, 23 (4) 125-132 (1976).

Les auteurs étudient dans cet article les compositions et les techniques d'application des revêtements céramiques pour haute température employés sur l'alliage de nickel et de molybdène et sur l'acier résistant à la chaleur, qui constituent les tuyères d'échappement du moteur à aviation.

Influence de certains variants sur les propriétés des céramiques à haute teneur en alumine.

S. Chatterjee, S. K. Guha, B. K. Sen et Sudhir Sen, *Cent Glass Ceram Res Inst Bull*, 23 (4) 132-136 (1976).

Les auteurs examinent dans cet article les variants comme la période de broyage, la dimension, la forme, la qualité de milieu de broyage; le type et la nature de la machine broyeuse en relation avec leurs influences sur les propriétés des compositions céramiques à haute teneur en alumine.

Une réduction de la teneur en Na_2O non seulement permet d'améliorer les propriétés électriques mais aussi elle contribue, d'une manière importante, à abaisser la température du frittage.

Influence d'additions de RO , R_2O_3 et RO_2 sur les verres $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ contenant MnO_2 .

H. A. El-Batal et N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, 23 (4) 136-143 (1976).

On détermine l'absorption optique et la susceptibilité

magnétique des verres de borate sodique. Dans le verre de base à (poids %) B_2O_3 80, Na_2O 20; Na_2O est substitué par 1, 5 et 10 parties de MgO , ZnO , CaO , SrO , BaO ou de CdO , et B_2O_3 est substitué par 2, 5, 10 et 15 parties de Al_2O_3 ou de SiO_2 .

Etude de quelques argiles de Jammu à l'aide de rayons infra-rouges.

S. N. Khosla, C. S. Gupta et R. K. Bedi, *Cent Glass Ceram Res Inst Bull*, 23 (4) 144-149 (1976).

Les auteurs ont effectué des dosages de six argiles provenant de la région de Jammu pour se rendre compte de leurs teneurs en minéraux. Le dosage montre que l'une de ces argiles contient de la montmorillonite. Une autre s'avère un mélange de trois minéraux, à savoir, kaolinite, illite et quartz; et le reste des argiles contient de la montmorillonite qui se trouve associée avec l'illite en proportion différente.

Glaçure plomb-borique ayant une solubilité faible.

Deuxième Partie. R. V. Lele et R. N. Ray, *Cent Glass Ceram Res Inst Bull*, 23 (4) 149-152 (1976).

Les auteurs ont développé une glaçure transparente ayant une composition moléculaire suivante: 0.110 K_2O , 0.086 Na_2O , 0.532 CaO , 0.106 BaO , 0.165 PbO , 0.286 Al_2O_3 , 3.300 SiO_2 et 0.386 B_2O_3 . Cette glaçure possède une longue plage de température de cuisson. Elle a aussi une bonne résistance à la rayure et à la craquelure.

Untersuchungen an Hochtemperatur-Keramik-Belags. N. Roy und S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **23** (4) 125-132 (1976).

Die Zusammensetzungen und die Technik zur Anwendung von den Hochtemperatur-Keramik-Belags, benutzt auf nimonische Leigerung und wärmebeständige Stahlkomponenten der Abgas-systeme von Düsenmaschinen, sind dargestellt.

Einfluß der Verfahrensvariable auf die Eigenschaften von hochtonerdehaltiger Keramik. S. Chatterjee, S. K. Guha, B. K. Sen und Sudhir Sen, *Cent Glass Ceram Res Inst Bull*, **23** (4) 132-136 (1976).

Verfahrensvariable wie Mahldauer, Korngröße, Form und Qualität des Mahlmittels; Typ und Beschaffenheit der Mahlanlage wurden, in Beziehung zu ihrer Wirkung auf die Eigenschaften von hochtonerdehaltigen Keramik-Zusammensetzungen, untersucht.

Verminderung im Na_2O -Gehalt verursachte nicht nur verbesserte elektrische Eigenschaften, sondern auch trug zum großen Teil zu einer bedeutenden Verminderung in der Sintertemperatur bei.

Der Einfluß von RO , R_2O_3 und RO_2 Zugabe auf MnO_2 -haltige $\text{Na}_2\text{O-B}_2\text{O}_3$ Gläser. H. A. El-Batal und N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **23** (4) 136-143 (1976).

Optischer Verlust und magnetische Suszeptibilität

von MnO_2 -haltigen $\text{Na}_2\text{O-B}_2\text{O}_3$ Gläsern wurden festgestellt. Im Grundglas B_2O_3 80, Na_2O 20 Gewichtsprozent 1.5 und 10 Gewichtsteil des Na_2O wurde durch MgO , ZnO , CaO , SrO , BaO oder CdO ersetzt und 2, 5, 10 und 15 Gewichtsteil des B_2O_3 wurde durch Al_2O_3 oder SiO_2 ersetzt.

Infrarot-Untersuchungen von einigen Töne aus Jammu. S. N. Khosla, C. S. Gupta und R. K. Bedi, *Cent Glass Ceram Res Inst Bull*, **23** (4) 144-149 (1976).

Infrarot-Untersuchungen von sechs Töne aus Jammu Bezirk wurden durchgeführt, um die Mineralkomponenten festzustellen. Einer der Töne bestand aus Montmorillonit. Der zweite Ton war eine Mischung von Kaolinit, Illit und Quarz. Die anderen Töne enthielten Montmorillonit, verbunden mit Illit in verschiedenen Mengenverhältnissen.

Eine Blei-Borsäure-Glasur mit niedriger Auslaugbarkeit. R. V. Lele und R. N. Ray, *Cent Glass Ceram Res Inst Bull*, **23** (4) 149-152 (1976).

Eine durchsichtige Glasur mit der Molekular-Zusammensetzung 0.110 K_2O , 0.086 Na_2O , 0.532 CaO , 0.106 BaO , 0.165 PbO , 0.286 Al_2O_3 , 3.300 SiO_2 und 0.386 B_2O_3 ist entwickelt worden. Diese Glasur hat eine weite Brandfeststrecke und gute Haarrissigkeits- und Ritzwiderstand.

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Correspondence : Editor, Central Glass and Ceramic Research Institute, Calcutta-700 032, India

STUDIES ON HIGH TEMPERATURE CERAMIC COATINGS

N. ROY AND S. S. VERMA*

Introduction

Metals are in general prone to corrosion even under the normal conditions of temperature and pressure when exposed to air, water and chemicals. Oxygen has been considered one of the primary agents of corrosion and in a recent study¹ corrosion has been attributed to the selective action of the electrons of the oxygen atom on the metal atoms of a body centred cubic structure. Heat is another primary corrosive agent. The corrosive effect is a direct function of the temperature to which the metal is exposed.

The demands of increasingly high temperatures in the aero-space technology, eg, 1400° in aero-engines and 7000° on external surface of re-entry space vehicles have been sought to be met broadly in two ways: (i) by using high temperature structural materials like alloy steels and refractory metals; cermets and intermetallic compounds and (ii) by using inorganic coatings of refractory metals or alloys; hardening the surface layer by conversion into boride, nitride, carbide and silicide, oxide coatings; and ceramic coatings²⁻⁶.

Considerable amount of work has been done for development of ceramic coatings on high temperature alloy parts of aero-engines and it has been established that these coatings can effect savings by the enhanced working life of the costly alloys and/or by the substitution of the costly alloys by cheaper ones^{7,8}.

This paper is confined to the research and development work carried out at the CGCRI on ceramic coatings using indigenous raw materials for the protection of nimonic alloy

and heat resistant steel parts of jet aircraft engines (Figs 1, 2).

Experimental

The experimental work has been carried out for developing ceramic coatings answering to the requirements of the end use in respect of the physical and chemical properties as well as suiting the thermal expansion and other properties of the base metals used in order to achieve a satisfactory adherence between the metal and the coating. In general, standard practice of processing has been used at different stages.

Base metals: The base metals used were largely confined to nickel based nimonic alloys for the aero-engine exhaust system parts (Table I, nos 1-4). In the case of the compressor stator blades a heat resistant steel alloy was used (Table I, no 5).

The metal parts were first degreased by means of trichlorethylene or by burning at about 700°. The metal surface was then rendered rough by uniblasting with bauxite powder. Alternatively, this could be done by using a bath of 10 per cent nitric acid and 2 per cent hydrofluoric acid followed by neutralisation in an alkali bath and rinsing in boiling water to free it first from the acid and then from the alkali remaining on the metal surface.

In the case of the heat resistant steel used for the compressor stator blades, the coating compositions being particularly suited to nimonic alloys, it is essential to adapt these to this material by a special treatment of nickel deposition and prefiring at 650°. This method has been developed for the direct application of white enamels to steel^{9,10} without the inter-

*Central Glass and Ceramic Research Institute, Calcutta-700 032, India

vening ground coat enamel. In this instance, this method helps to overcome the wide thermal expansion gap between the steel and the coating and otherwise also promotes adherence between the two components. The requirements in the stator blades are that the coating should protect it from the action of salt spray and abrasive

particles, *eg*, sand.

Ceramic coatings: Although the term 'ceramic coating' theoretically covers 'vitreous enamels', in usage the latter term signifies a primarily glassy coating fused on metals at comparatively low temperatures (usually below 900°), while the former denotes a more refractory coating,

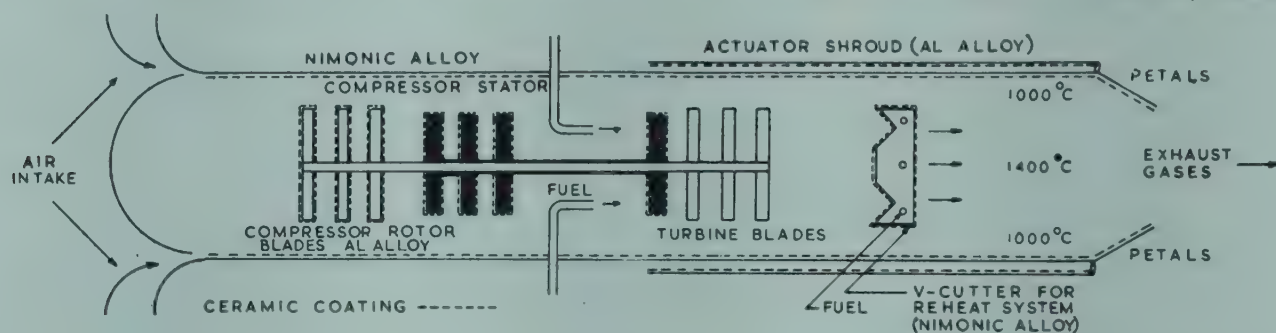


Fig 1
Use of ceramic coatings on different parts of jet aircraft engine

TABLE I

Compositions of base metal alloys

Constituents	Proportions in weight per cent				
	1	2	3	4	5
Carbon	0.08-0.15	0.13 max	0.10	0.10 max	0.12
Silicon	1.00 max	1.15 „	0.80	0.80	2.25-3.25
Copper	0.50 „	—	—	—	—
Iron	5.00 „	5.00 „	4.00	8.00	Base
Manganese	1.00 „	1.00 „	0.50	0.40	2.75-4.00
Chromium	18-21	18-21	23-26	19-22	11.5-14.0
Titanium	0.2-0.6	1.8-3.0	—	0.35-0.75	—
Aluminium	—	0.8-2.0	0.5 max	0.35	—
Cobalt	—	15-21	—	—	—
Nickel	Base	Base	Base	Base	3.75-4.75
Tungsten	—	—	13-16	—	—
Sulphur	—	—	0.013	0.012 Max	—
Phosphorous	—	—	„	0.02 „	—
Molybdenum	—	—	—	1.8-2.3	—
Niobium	—	—	—	0.9-1.3	—



Fig 2

Ceramic coated compressor stator blades

the glassy phase playing only a secondary role, viz, that of bonding the refractory coating materials⁶.

The efficiency of a ceramic coating as a barrier between the base metal and the corrosion agents requires that firstly it should possess high resistance against heat, chemicals, erosion, oxidation, etc, and secondly it should be so processed as to produce a good adherence with the metal and present a continuous and non-porous coating. These properties are achieved by taking advantage of the characteristics of the various components used in forming the glass part on the one side and the refractory materials used as mill additions, on the other. In general, calcium-barium-borosilicate glasses, with and without the inclusions of chromium oxide and minor amounts of titanium oxide, magnesium oxide, aluminium oxide and manganese dioxide were found to give good results. In the mill additions zirconia and alumina showed the best heat resistance but rather poor thermal shock resistance. Chromium oxide was, therefore, used as the best compromise in respect of these two properties which have a very important bearing on the success or failure of the ceramic coating.

Preparation of the ceramic coating: Standard practice of frit preparation, milling, etc, were followed. Compositions found to yield the best results are shown in Table II.

Application of the ceramic coating: After wet grinding the coating slip was passed through a 200 mesh IS sieve. The slip was then applied on the pre-treated base metal either by spraying or dipping, dried slowly and then fired in a muffle

furnace at the required temperature. The specific gravity of the slip was adjusted at 1.6 to 1.7 for spraying and at about 1.8 for dipping. The application of the slip was such as to yield a fired application weight of not more than 0.86 gm per sq decimetre. Thicker coatings were liable to chip off after firing.

Testing procedure

The testing procedure used was essentially the one proposed by B. L. Paris⁸, though minor variations were made where considered necessary. The properties of the coating tested were those required for satisfactory performance under service conditions.

Adherence: This property was tested by bending a flat piece of the coated metal (size 10 cm × 3 cm and thickness of metal 0.07 to 0.12 cm) slowly through an angle of 180°, when chipping of the coating should not occur except at the edges and on the reverse side. Alternately, the Porcelain Enamel Institute (PEI) method may be followed which consists of first deforming the sample in a press at 907 kg pressure and then determining the proportion of the surface still left coated¹¹.

The heat resistant steel stator blades used, had a cylindrical surface with a maximum thickness of 0.14 cm along the central axis. This was, therefore, subjected to the PEI impact test, which determines the minimum impact required for chipping the coating on cylindrical surface. PEI standard requirement for 0.14 cm thickness is 0.008 kg/m.

Thermal shock resistance: This property of a coating is a measure of its capacity to withstand repeated heating and cooling which may be in some respect even more important than heat endurance. The method consists of first heating the coated part to its operating skin temperature (about 700°), keeping it at that level for 20 minutes and then quenching it in water at room temperature. This cycle is thus repeated.

Extended heating resistance: This test was meant to determine the degree to which the coating will stand high temperature conditions, where

the temperature and time may be the variables. It comprises heating at 93.6° above its operating skin temperature in an electric muffle furnace in static condition for 60 minutes, keeping the switch off for next 60 minutes and thus repeating

the cycle three times. In the next cycle the heating is repeated but the soaking is carried on for 4 hours. The operation is thus repeated for a total of 20 days (200 hours).

Chemical resistance against acid and alkali: In

TABLE II

Preparation and processing details of ceramic coatings

		Coating composition weight per cent		
		(A)	(B)	(C)
(a) Batch compositions:				
Quartz power (−200 mesh)		32.00	43.00	25.00
Barium carbonate		47.00	24.00	38.00
Boric acid		9.00	11.00	7.00
Calcium carbonate		6.00	3.00	4.00
Beryl powder (−200 mesh)		2.00	—	—
Zinc oxide		4.00	3.00	3.00
Titanium dioxide		—	7.00	—
Magnesium carbonate		—	3.00	—
Aluminium oxide		—	4.00	—
Potassium nitrate		—	2.00	—
Chromium oxide		—	—	20.00
Manganese dioxide		—	—	3.00
(b) Melting temperature (°C)		1300	1300	1350
Coating slip compositions				
	Ni-1	Ni-2	Sl-2	Sl-6
(c) Mill batch				
Frit composition (A)	100.00	100.00	—	70.00
“ “ (B)	—	—	—	30.00
“ “ (C)	—	—	100.00	—
Chromium oxide	15.00	40.00	—	15.00
Clay	5.00	5.00	5.00	5.00
Water	50.00	50.00	50.00	50.00
(d) Firing temperature (°C)	950-1000	1150-1180	1000-1050	950-1000
(e) Nature of coating finish after firing	glossy	glossy	matt	glossy

this test the coating was tested for its resistance against boiling citric acid, 6 per cent for 2½ hours and against boiling sodium pyrophosphate solution, 1 per cent for 2 hours. The result was expressed in terms of weight loss in gm per sq decimetre.

Salt water test: This was a test for determining the resistance against corrosion by salt water and was carried out for 100 hours using a 5 per cent salt solution.

Skin temperature test: This test has been devised for determining the thermal insulating property of the coating and is carried out on a sample coated on one side only. The coated side is heated by a bunsen flame and the temperature on both sides is measured by means of thermocouples. This property is directly related to the thermal conductivity of the coating.

Thermal conductivity: This property was measured by the divided bar method¹³ on a sample

TABLE III

Results of tests on ceramic coated laboratory specimens

Tests	Coating slip compositions			
	Ni-1	Ni-2	Sl-2	Sl-6
1. Adherence				
(a) Flat piece, nimonic alloys	Good	Good	Good	Good
(b) Stator blade, heat resistant alloy steel, PEI pendulum impact test	0.085 Kg/m	—	—	—
2. Thermal shock	No chipping but gloss slightly affected after ten cycles	No chipping and no effect on gloss after ten cycles	Chipping after four cycles	Chipping after six cycles
3. Extended heating	Slight effect on gloss only	No effect	No effect	No effect
4. Chemical resistance (weight loss in gm/dm ²)				
(a) Acid resistance	0.04805	0.00775	0.04495	0.00620
(b) Alkali resistance	0.04340	0.00186	0.02790	0.00252
5. Salt water test	No effect	No effect	No effect	No effect
6. Skin temperature test—				
hot face (°C)	1100	1100	1100	1100
Cold face (skin) (°C)	700	700	800	760
7. Thermal conductivity: K value in gm cal/sec/°C/cm, with hot face temperature of:				
100	0.00390	—	—	0.0047
200	0.00420	—	—	0.0051
300	0.00450	—	—	0.0054
400	0.00520	—	—	0.0057

of size $4\text{cm} \times 4\text{cm}$, having a coating on both sides, the application weight being 0.85 gm/dm^2 . The thicknesses of the metal and the coating being 0.1230 cm and 0.0046 cm respectively.

Results and discussions

The results of the tests are shown in Table III, on the four coating slip numbers (Ni-1, Ni-2, Sl-2 and Sl-6) referred to in Table II.

It is observed from the results that while all the four coating slip compositions (Ni-1, Ni-2, Sl-2 and Sl-6) have shown good performance in respect of adherence and extended heating tests, the thermal shock test brought out considerable variation between the two compositions 'A' (used in coating slips Ni-1 and Ni-2) and 'C' (used in coating slips Sl-2 and Sl-6), the third composition 'B' having been used only in a small proportion in the slip Sl-6. The two slips of the first series (Ni-1 and Ni-2) comprising a calcium-barium-borosilicate glass system with small proportions of zinc and beryl along with mill added chromium oxide varying between 15 and 40 per cent, showed decidedly better thermal shock resistance than the slips Sl-2 and Sl-6 of the second series which comprise somewhat less proportion of the calcium-barium-borosilicate glass with inclusion of small proportions of manganese and zinc but high proportion of chromium and without any chromium in the mill additions in one case (Sl-2) and practically the same basic and mill compositions as were used in the first series (Ni-1 and Ni-2), in the other case (Sl-6). Better performance of the composition 'A' with high chromium in the mill addition was also borne out by the comparative results of the two slips (Sl-2 and Sl-6) in the second series, wherein slip Sl-6 (comprising 70 per cent composition 'A' plus mill added chromium) showed appreciably better result than slip Sl-2, although on the whole the second series showed inferior performance to that of the first series (Ni-1 and Ni-2).

The skin temperature is the temperature of the external surface of the jet pipe, the inside of which is exposed to the high temperature of

flame and flue gases of the jet. Skin temperature should not exceed safe limits, otherwise the whole metal structure may collapse. It is seen from the results of this test (Table III) that the coating slips of Ni-series (Ni-1 and Ni-2) were decidedly better than those of Sl-series (Sl-2 and Sl-6). Slip composition Sl-6 came within tolerable limits. As will be evident from the thermal conductivity values for the Ni-1 and the Sl-6 slip compositions, the two properties of thermal conductivity and skin temperature are directly related to each other. It is, therefore, obvious that the thermal conductivity value of the ceramic coating should be sufficiently low in order that the temperature of the skin on the reverse side does not exceed the safe limit. At the same time it should not be so low as to adversely affect the thermal shock resistance and to cause the development of dangerous tensile strains in the ceramic coating due to very slow rate of conduction of heat through it, while the skin is rapidly cooled.

The results of the tests for thermal properties, are also corroborated by a consideration of the thermal properties of the constituents^{5,12} of the coating compositions. The two slips Ni-1 and Ni-2, showing the best performance, were based on the coating composition 'A' comprising CaO-BaO-SiO_2 in which the high proportion of BaO played a very important role due to its very low thermal conductivity value. While chromium occupied a medium position in respect of this property, its use in the free form as in mill addition seemed to favour low thermal conductivity of the coating but not so when included in the glass as was shown by the high skin temperature of the slip Sl-2 (basic composition 'C' in which all the chromium is present in the form of glass and none in the free uncombined form). The performance of the slip Sl-2 may also be partly attributed to somewhat low proportion of barium. The intermediate position of slip Sl-6 (using 70 per cent composition 'A' and 30 per cent 'B') was also explainable on the basis of high barium in 70 per cent of the composition 'A', low thermal conductivity of titanium present

in 30 per cent of the composition B and presence of chromium in the free form.

In regard to the chemical properties of resistance against corrosion by salt water, boiling acid and boiling alkali, it is observed that all the four coatings satisfy the requirements of salt water test. As regards resistance against acid and alkali, the improvement from slip Ni-1 to Ni-2 appears to be due to the increase in mill added chromium (from 15 to 40 per cent). On the other hand, high acid and alkali resistance values (equal to those of Ni-2) of slip SI-6 seems to be due to the fact that 30 per cent of the basic composition 'B' used, comprised high silica in combination with zinc oxide and titania. The performance of slip SI-2 being at par with that of Ni-1 may be attributed to the presence of low proportion of silica, all chromium in combined form and absence of titania in the basic composition 'C' on the one hand and the absence of free chromium on the other.

Production and utilisation

Utilising the results of the above investigations, production was started at the Institute on a small scale for supply to some government organisations and undertakings engaged in aero-engines research and development and manufacture of aircraft. Preliminary reports of performance were satisfactory.

Summary

Ceramic coatings suitable for the effective protection of nimonic alloys and heat resistant steels for use under the operating conditions of jet aero-engines were produced from raw materials indigenously available in the country.

Thermal properties essential for protection of the metal structure and maintenance of skin temperature within safe limits were obtained in the ceramic coatings by taking advantage of the low thermal conductivity characteristics of barium oxide and titania on the one hand and of chromium oxide used in an uncombined form on the other.

Suitable refractory properties of the ceramic coatings could be achieved by the incorporation of silica, calcia, zinc oxide and titania in the glassy phase and chromium oxide as a refractory mill addition.

Resistance of a high order against corrosion by salt water and boiling acid and alkali of the ceramic coating was achieved by a combination of silica, titania, zinc oxide in the calcia-baria-borosilicate glass and the use of chromium oxide in the free state in mill addition.

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EFFECT OF PROCESSING VARIABLES ON THE PROPERTIES OF HIGH ALUMINA CERAMICS

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Introduction

Alumina is one of the principal raw materials used in electrical, electronic and engineering ceramics developed in recent years.

The high maturing temperature of alumina ceramics can be brought down to a commercially viable range by using finely ground material to facilitate the solid state reaction. The reaction

can be further accelerated by incorporating suitable sintering aids.

F. H. Norton and W. D. Kingery¹ observed that grain size of 50-150 micron of alumina did not sinter even at 2000°. E. Ryshkewitch² suggested that the grain size of 10-12 micron of alumina would result in good sintering. W. D. Kingery³ observed that the rate of sintering of alumina either in solid phase or in liquid phase is inversely proportional to the grain diameter.

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Alumina, as obtained from Bayer's process, when calcined at a temperature of 1550°, converts mostly to alpha corundum and the hardness reaches as high as 9 in Moh's scale. Pot mill or ball mill grinding with alumina balls as grinding media is still very widely used for grinding even though the method is a very time consuming one. Vibro energy mill or fluid energy mill (jet mill) grinding are much more efficient than pot mill or ball mill grinding so far as the time factor is concerned. Bayer's alumina contains Na₂O, which deteriorates the electrical properties of the final product. Sodium free alumina is, therefore, preferred in electrical or electronic ceramics.

Alumina being very hard, long hours of grinding and contamination during grinding are unavoidable. A study on grinding schedule and the resulting contamination and its effect on the physical and electrical properties of the alumina ceramics was undertaken.

Experimental

Technical alumina was calcined at 1550° for two hours. Chemical analyses of the technical alumina as received and after calcination are

given in Table I. The calcined alumina was ground in pot mill with alumina balls as grinding media for 30, 42 and 50 hours and it was also separately ground in the vibro energy mill with zircon porcelain as grinding media for 6, 12, 18 and 24 hours. The particle size distributions of

TABLE I

Chemical analysis of uncalcined, calcined and soda removed alumina

Constituent (%)	Technical alumina as received	Calcined and vibro energy mill ground alumina (2 hours grinding)	Calcined and then treated for Na ₂ O free alumina
Al ₂ O ₃	95.19	97.23	Na ₂ O con-
SiO ₂	0.20	0.30	tent reduced
Fe ₂ O ₃	0.07	0.14	to 0.11 per
TiO ₂	Tr	Tr	cent by che-
CaO	—	1.00	mical proce-
MgO	0.26	0.26	ssing
K ₂ O	nil	nil	
Na ₂ O	0.59	0.53	
ZrO ₂	nil	0.21	
LOI	3.47	0.96	

TABLE II

Particle size distribution (per cent) as obtained on grinding calcined alumina by vibro energy mill and pot mill for different periods of grinding time

Particle size in micron	Ground in vibro energy mill (hrs)				Ground in pot mill (hrs)		
	6	12	18	24	30	42	50
25	3.3	nil	nil	nil	nil	nil	nil
25-15	0.4	nil	nil	nil	nil	nil	nil
15-10	2.9	nil	nil	nil	2.3	2.0	2.0
10-8	5.4	nil	nil	nil	11.0	1.8	5.8
8-5	9.0	2.0	4.0	3.0	11.5	3.2	13.8
5-3	15.0	5.9	2.0	2.3	14.4	10.0	19.4
3-2	7.0	7.7	5.8	3.9	20.8	14.0	16.1
2-1	23.0	42.4	36.8	32.8	26.0	43.0	29.7
1.0-5	29.2	32.0	37.0	32.0	9.8	25.0	9.9
0.5	4.8	10.0	26.0	26.0	3.2	2.0	3.1

the ground material as determined by Andreasen's pipette method are given in Table II.

A series of compositions (A_1 , A_2 , A_3 and A_4) of 94 per cent alumina content was prepared with six per cent additives. The alumina for this series was ground in vibro energy mill. The other series of compositions (B_1 , B_2 and B_3) containing 98.5 per cent of calcined alumina were prepared from the vibro energy mill ground, pot mill ground and soda free pot milled alumina respectively (Table III).

All these compositions (Table III) were dried and pressed in the form of 57 mm dia \times 3 mm discs using 0.5 per cent of polyvinyl alcohol and 4 per cent of water as binder (8000 psi). The discs were fired at 1600° for four hours.

Another series of compositions C_1 and C_2 (Table III) were also prepared with processed alumina, pot mill ground, having 94 and 96 per cent of Al_2O_3 content in the final products. Pressed discs of C series (Table III) were found to sinter fully when fired at 1500° with four hours of soaking.

Physical properties like density, water absorption, firing shrinkage and fired colour were

determined and the results are shown in Table IV.

Power factor, dielectric constant, loss factor were made on these discs using Boomton Q-meter at a frequency of 1 megacycle/sec. Electrical strength was determined in 100 kV transformer, volume resistivity was measured on Spinlab electrometer at room temperature (25°) and at a relative humidity of 52 per cent. The results are given in Table V.

Variation in electrical properties amongst the different types of samples of one single composition was also studied. Studies on electrical properties of a composition of 94 per cent pot mill ground alumina content were made on four different samples and the results are given in Table VI.

Results and discussion

Table II shows that the particle size gradually decreased with the increase in the grinding period either by vibro energy mill or pot mill. It was also noticed that vibro energy mill grinds much quicker in comparison to that by the pot mill. Table I indicates that there is a contamina-

TABLE III
Alumina compositions prepared from calcined and treated alumina

Composition	Calcined Al_2O_3 ground in vibro energy mill		Calcined Al_2O_3 ground in pot mill		Soda removed Al_2O_3 ground in pot mill		Other constituents (%)
	Grinding time (hrs)	Per cent	Grinding time (hrs)	Per cent	Grinding time (hrs)	Per cent	
A_1	6	94	—	—	—	—	6
A_2	12	94	—	—	—	—	6
A_3	18	94	—	—	—	—	6
A_4	24	94	—	—	—	—	6
B_1	2	98.5	—	—	—	—	1.5
B_2	—	—	50	98.5	—	—	1.5
B_3	—	—	—	—	50	98.5	1.5
C_1	—	—	—	—	50	94.0	6
C_2	—	—	—	—	50	96.0	4

tion of ZrO_2 and SiO_2 during grinding in vibro energy mill due to the wear and tear of zircon porcelain grinding media.

On studying the physical properties (Table IV) and the electrical properties (Table V) for the compositions A_1 , A_2 , A_3 and A_4 , it was observed that although the density increased due to increasing grinding time in vibro energy mill, the electrical properties gradually deteriorated. This was presumably due to the increasing contamination by ZrO_2 and SiO_2 picked up from the grinding media. On the other hand, B_2 (the composition with pot milled alumina) when compared with B_1 (the composition with vibro energy milled alumina) showed improved electrical properties.

The reduction of Na_2O associated with Bayer's alumina by 0.42 per cent caused an appreci-

TABLE IV

*Physical properties of the alumina composition fired at *1600° in oil fired furnace for four hours*

Composition	Density	Water absorption (%)	Firing shrinkage (%)	Fired colour
A_1	3.66	nil	15.9	white
A_2	3.71	nil	16.0	dull white
A_3	3.71	nil	16.0	"
A_4	3.73	nil	16.1	creamish white
B_1	3.78	nil	16.0	white
B_2	3.75	nil	16.0	white, translucent
B_2	3.81	nil	25	"
C_1	3.62	nil	16.0	"**
C_2	3.80	nil	16.0	"

* C_1 and C_2 were fired at 1500° with four hours soaking
**Surface finish was very good

TABLE V

Electrical properties of the alumina compositions*

Composition	Power factor at 1 mcs (%)	Dielectric constant	Loss factor at 1 mcs (%)	Resistivity (Ohm-cm)	Electrical strength (kV/mm)
A_1	0.019	14	0.275	1.7×10^{14}	16.5
A_2	0.14	14.3	1.96	1.3×10^{14}	14.5
A_3	0.23	12.5	2.92	1.72×10^{14}	14.34
A_4	0.74	14.65	10.87	2.87×10^{14}	16.5
B_1	0.066	12.19	0.73	3.58×10^{14}	18.58
B_2	0.034	12.21	0.4	3.6×10^{14}	19.33
B_3	0.022	10.16	0.23	7.25×10^{14}	13.5
C_1	0.032	13.0	0.38	2.37×10^{13}	19.0
C_2	0.029	13.06	0.37	2.83×10^{13}	20.0

*at room temperature 25°, relative humidity 48 per cent

TABLE VI

Variation of electrical properties in different samples of alumina composition A

Sample	Power factor (%)	Dielectric constant	Loss factor (%)	Resistivity (Ohm-cm)	Electrical strength (kV/mm)
1	0.087	11.61	1.11	3.67×10^{15}	13.8
2	0.039	10.40	0.41	3.49×10^{15}	12.2
3	0.075	11.30	0.85	7.25×10^{15}	11.4
4	0.056	10.45	0.58	8.12×10^{15}	10.9

able improvement in electrical properties of the alumina compositions B₃, C₁, C₂ (Table V).

Variation in electrical properties (Table VI) from sample to sample in the same composition A could mostly be due to non-homogeneity in mixing and variations in subsequent steps. Variation in closed pores and laminations inside the samples might be the possible reasons for such variations.

Summary

Vibro energy mill grinding could be adopted provided the pure and high density alumina grinding media was used. The solid state reaction was facilitated and much improved electrical

properties were obtained by cutting off the contaminants by using very high density Zertex brand grinding media or recrystallised alumina grinding media.

The removal of Na₂O from the Bayer's alumina showed a marked improvement in the electrical properties. Further removal of the impurities would definitely ensure much improvement in the electrical properties as well as in the overall sintering temperature.

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THE EFFECT OF RO, R₂O₃ AND RO₂ ADDITIONS ON MnO₂ CONTAINING Na₂O-B₂O₃ GLASSES

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Introduction

Manganese, which is a member of the transition metals, behaves as a glass colourant, and also can play a role as a decolouriser¹. The colour produced in glass by manganese ions depends on the equilibrium between the faint Mn²⁺ ions and the deep purple Mn³⁺ ions.

A. Paul and D. Lahiri² found that the man-

ganese ions equilibrium shifted more towards the oxidised state when the alkali oxide concentration in binary alkali borate glasses increased and/or when the basicity increased.

The characteristics of the optical absorption bands due to the manganese ions in glasses were studied by several authors¹⁻¹⁴. The broad band due to the Mn³⁺ ions is attributed to the spin-allowed^{3,5,6,10-14} transition $5\bar{3} \rightarrow 5\bar{5}$.

The attribution of the four spin-forbidden

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weak bands of the Mn^{2+} ions varies with the symmetry of the ions whether they occupy octahedral or tetrahedral coordination⁸.

In previous publications¹⁰⁻¹⁴, the authors have shown a marked splitting of the broad band of Mn^{3+} ions in a series of alkali borate, lead borate and lead silicate glasses.

In the present work, a study is made on the effect of introducing divalent, trivalent or tetravalent metal oxides on the absorption spectra and paramagnetic character of borate glasses containing manganese.

Experimental

The glasses were prepared with chemically pure grade materials. The boric oxide was introduced as boric acid and soda in the form of soda ash. Manganese was added to the batch as MnO_2 . The glasses were melted in platinum-2 per cent rhodium crucibles in electrically heated muffle furnaces under normal atmospheric conditions. The melting was performed at 1000° and continued for four hours. For the transmission measurements, the glasses were cast into rectangular moulds 1 cm^2 in cross section and 4 cm length. For the magnetic susceptibility, rods were cast of about 10 cm length and 1 cm^2 cross section. The absorbance results obtained by Beckman DR spectrophotometer were plotted as the molecular extinction coefficient against the corresponding wavelength and is calculated as follows^{5,11}:

$$E_M = \frac{OD}{M \times L}$$

where OD was the optical density at the particular wavelength of a sample of thickness L cm, and M the concentration of the transition metal ion in mole/1000 cm^3 of the glass.

The magnetic susceptibility of the manganese ions in glass was determined by the Gouy method using the coloured and the corresponding blank glass. The susceptibility was measured at field strength of approximately 12,000 gauss. The volume susceptibility was calculated from the equation:

$$\begin{aligned} \delta_s &= \frac{1}{2}(K_s - K_o) A(H^2 - H_o^2) \\ &= \frac{1}{2}(K_s - K_o) \frac{S}{l\sigma_o} (H^2 - H_o^2) \end{aligned}$$

where δ_s was the resultant magnetic pull on the specimen; K_s and K_o the respective susceptibilities of the specimen and air; A the cross-sectional area of the specimen; S, σ_o , l the mass, the density and the length of the specimen respectively. The mass susceptibility of the manganese ions was then calculated.

Results

Effect of the divalent metal oxides: The effect of the divalent metal oxides was studied by replacing 1, 5, or 10 parts of soda by one of the divalent alkaline earth oxides MgO, ZnO, CdO, CaO, SrO or BaO in the composition B_2O_3 80, Na_2O 20 per cent containing 0.20 gm MnO_2 per 100 gm melt (Table I).

The results obtained (Figs 1 to 3) can be summarised as follows.

TABLE I

Compositions and magnetic susceptibility of alkali borate glasses containing 0.20 gm MnO_2 . Base composition B_2O_3 80, Na_2O 20 wt per cent. 1, 5 or 10 parts of soda replaced by the divalent oxides MgO, ZnO, CaO, SrO, BaO or CdO

Glass	Composition (wt per cent)			Mass susceptibility ($\chi \times 10^6$)
	B_2O_3	Na_2O	RO	
1	80	19	MgO 1	0.1126
2	80	15	5	0.0657
3	80	10	10	0.0996
4	80	19	ZnO 1	0.1311
5	80	15	5	0.0930
6	80	10	10	0.1203
7	80	19	CaO 1	0.0727
8	80	15	5	0.0727
9	80	10	10	0.0898
10	80	19	SrO 1	0.1074
11	80	15	5	0.0857
12	80	10	10	0.0994
13	80	19	BaO 1	0.1106
14	80	15	5	0.0941
15	80	10	10	0.1204
16	80	19	CdO 1	0.1504
17	80	15	5	0.0961
18	80	10	10	0.1281

Glasses containing one part of the divalent alkaline earth oxides (Fig 1): The glasses containing MgO, ZnO and CaO showed one broad triple-split band. The peaks of this band occurred around 480, 500 and 540 $m\mu$

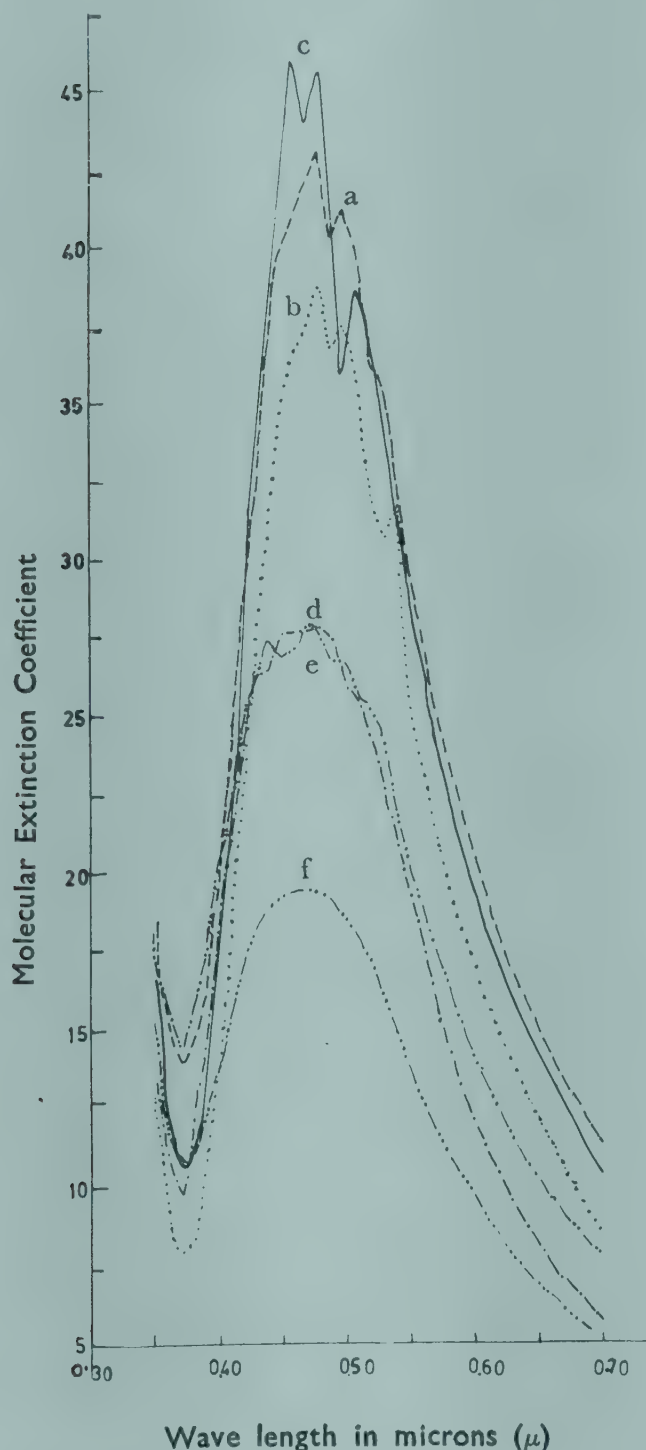


Fig 1
Molecular extinction coefficient of: a—glass 1, b—glass 4, c—glass 7, d—glass 10, e—glass 13, f—glass 16 of Table I

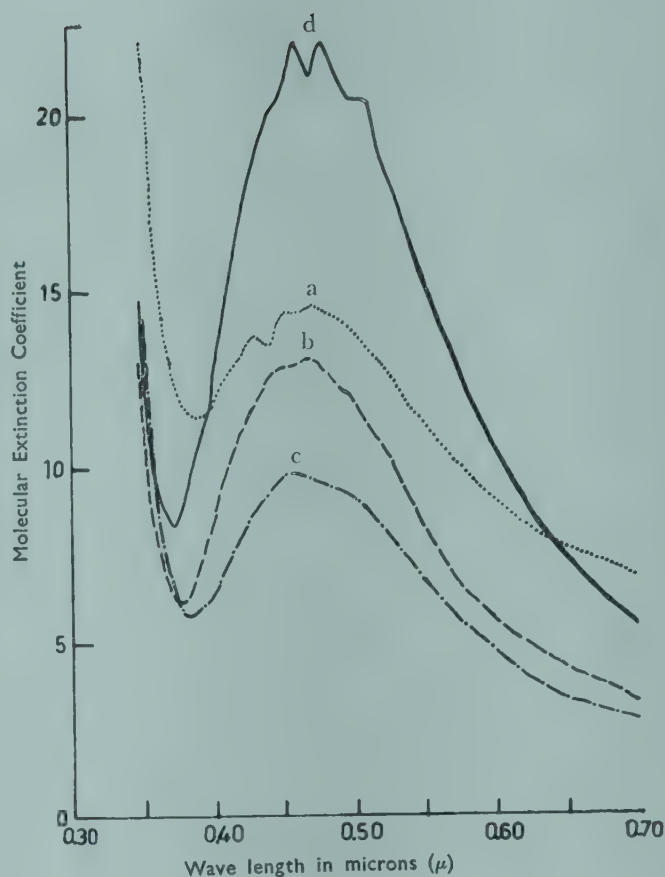


Fig 2
Molecular extinction coefficient of: a—glass 2, b—glass 5, c—glass 8, d—glass 14 of Table I

in the MgO and ZnO glasses; and at 460, 480 and 510 $m\mu$ for the glass containing CaO. The molecular extinction coefficients of these peaks were approximately 43 for the first peak and decreased progressively in intensity for the second and the third peaks. The glasses containing either strontium, barium or cadmium oxides showed one broad symmetrical band with a maximum around 470 $m\mu$. The molecular extinction coefficients of the bands maxima was about 28 for the strontium or barium oxides glasses, and 19.5 for the glass containing cadmium oxide.

Glasses containing five parts alkaline earth oxides (Fig 2): The glasses containing MgO, ZnO and CaO showed broad symmetrical band with small peaks at about 450, 470 and 500 $m\mu$. The molecular extinction coefficients of the bands maxima were 14.5, 13 and 9.7 for zinc oxide, magnesia and lime glasses respectively.

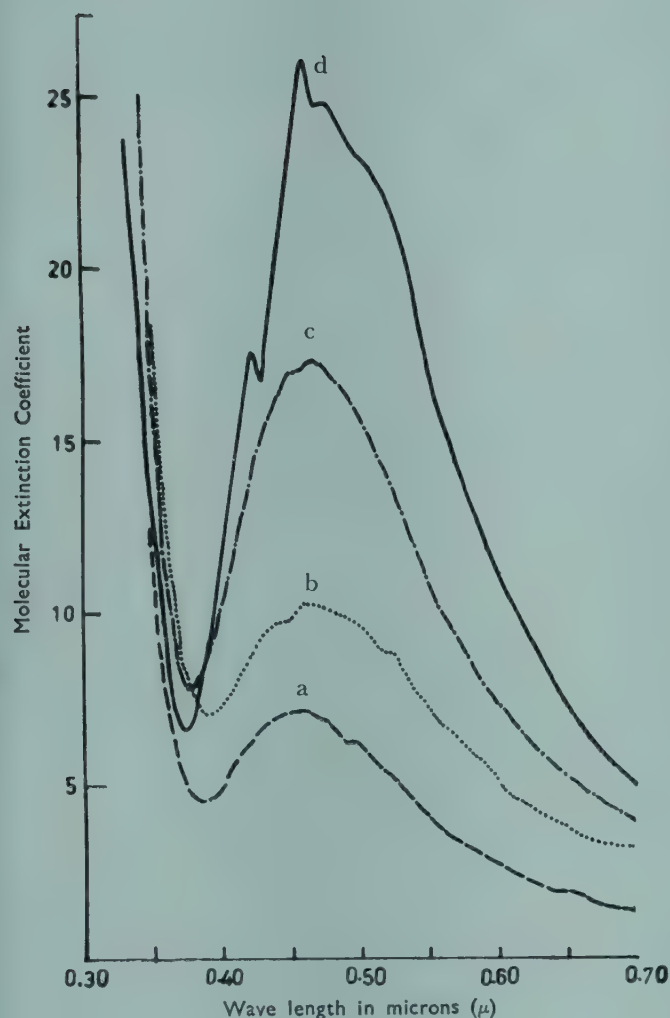


Fig 3

Molecular extinction coefficient of: a—glass 3, b—glass 6, c—glass 9, d—glass 15 of Table I

The glass containing BaO showed highly resolved triple-split band with peaks at 460, 480 and 510 $m\mu$. The molecular extinction coefficient of the band maximum was 22.

Glasses containing ten parts alkaline earth oxides (Fig 3): The glasses containing MgO, ZnO and CaO showed one broad symmetrical band with small unresolved peaks around 450, 470 and 500 $m\mu$. The molecular extinction coefficients of the bands maxima were 7.2, 10.2 and 12.3 for the glasses containing MgO, ZnO and CaO respectively. The glasses containing BaO showed highly resolved triple-split band with peaks at 460, 480, and 510 $m\mu$. The molecular extinction coefficient of the band maximum was 26. A small band was observed at 420 $m\mu$ with molecular extinction coefficient of 17.5.

Magnetic susceptibility: The replacement of 1 or 5 parts soda by any of the divalent metal oxides decreased the paramagnetic susceptibility of the glass (Table I). Replacements of 10 parts of alkali oxide by divalent metal oxides increased the paramagnetic susceptibility. The order of the effect of the divalent metal oxides can be arranged as follows: CdO (highest), ZnO, MgO, BaO, SrO and CaO (least).

Effect of trivalent and tetravalent metal oxides :

Effect of alumina: The replacement of 2, 5, 10 or 15 parts of boric oxide by alumina in the glass of B_2O_3 80, Na_2O 20 wt per cent containing 0.20 gm MnO_2 per 100 gm glass was made (Table II). The extinction curves (Fig 4) showed one broad symmetrical band with two splitted peaks at 455 and 470 $m\mu$. The molecular extinction coefficients of the bands maxima decreased considerably with the first addition of alumina and then slightly increased with the increase in the alumina content.

Effect of silica: The replacement of 2, 5, 10 or 15 parts of boric oxide by silica was made in the glasses (Table II). Fig 5 shows that there was one broad almost symmetrical absorption band. The molecular extinction coefficients first decreased and then remained nearly constant.

Magnetic susceptibility: The paramagnetic

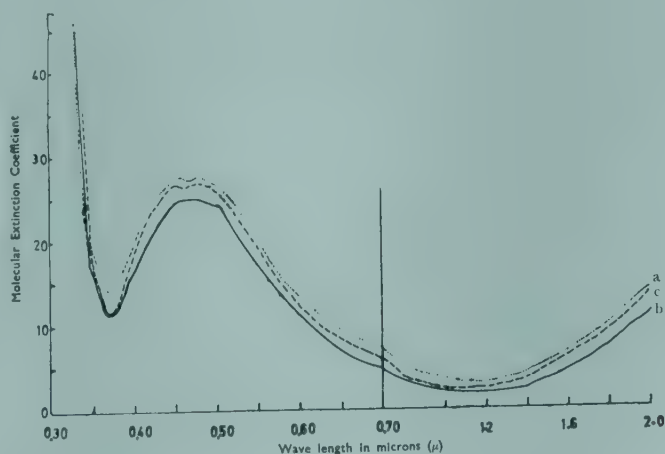


Fig 4

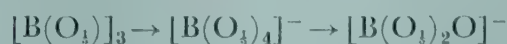
Molecular extinction coefficient of: a—glass 19, b—glass 20, c—glass 21 of Table II

susceptibility of the glasses increased with silica more than that with alumina (Table II).

Discussions

Condition of manganese ions in borate glasses: In glasses containing manganese, equilibrium is established between manganous and manganic ions depending on the composition of the base glass and the melting condition.

In binary alkali borate glasses, the absorption spectra and coordination number of most transition metal ions change significantly around 20-25 per cent alkali oxide^{1,4-6,10,11,15}. Nuclear magnetic resonance investigations¹⁶ on alkali borate glasses have shown that when alkali oxides are added to molten oxide, the sequence of the reactions involved is:



This can be explained by assuming that the addition of R_2O to B_2O_3 is equivalent to an acid-base titration in which acidic $[\text{B}(\text{O}_{\frac{1}{2}})_3]$ triangles are neutralised stepwise by the alkali oxides. The first neutralisation product is a $[\text{B}(\text{O}_{\frac{1}{2}})_4]^-$ tetrahedron which may be termed as mildly basic. When more alkali oxide is added, the more basic $[\text{B}(\text{O}_{\frac{1}{2}})_2\text{O}]^-$ groups are formed. The higher basicity of a $[\text{B}(\text{O}_{\frac{1}{2}})_2\text{O}]^-$ group (SP 2 hybrid) can be related to the availability

TABLE II

Composition and magnetic susceptibility of alkali borate glasses of the composition B_2O_3 80, Na_2O 20 wt per cent containing 0.20 gm MnO_2 per 100 gm glass, with parts of the boric oxide replaced by alumina or silica

Glass	Composition (wt per cent)			Mass susceptibility ($\chi \times 10^6$)
	B_2O_3	Na_2O		
19	78	20	Al_2O_3 2	0.2100
20	75	20	5	0.2111
21	70	20	10	0.2132
22	65	20	15	0.2150
23	78	20	SiO_2 2	0.2120
24	75	20	5	0.2164
25	70	20	10	0.2212
26	65	20	15	0.2281

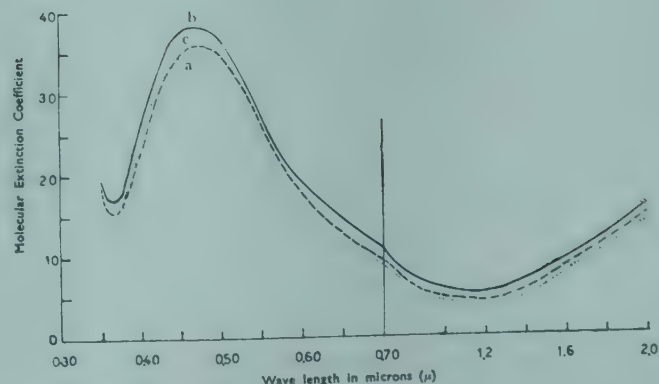


Fig 5
Molecular extinction coefficient of: a—glass 24, b—glass 25, c—glass 26 of Table II

of excess electrons. In the tetrahedral configuration this electron is involved in the hybrid orbitals, whereas in the triangular group it is not. Thus, the donor property or the oxygen ligands associated with it is less than that of the non-bridging oxygen associated with the $[\text{B}(\text{O}_{\frac{1}{2}})_2\text{O}]^-$ groups.

Attribution of the absorption band intensity: The increase of the intensities of the observed bands can be correlated with the increase in the basicity of the glass. The observation of a change around 20 per cent R_2O is presumably related to: (i) structural transformation due to the formation of diborate groups at the expense of pentaborate pairs¹⁶; (ii) variation of the fraction of 4-coordinated borons with composition; (iii) increase of the covalency in the metal-oxygen bonds; or (iv) increase in the alkali oxide concentration simplifies the spectrum and increases the intensity of the d-d bands. The enhanced intensity of the absorption bands indicates larger distortion of the already distorted Mn^{3+} ions. This extra distortion produces more asymmetry and shifts the band maximum further away from the centro-symmetric group and this produces a higher intensity in the d-d band.

Attribution of the number and position of the bands and the reasoning for the observed splitting: The main absorption band of the glasses containing manganese melted under atmospheric condition is believed to come from $5\bar{3} \rightarrow 5\bar{5}$ transition of Mn^{3+} ions in octahedral symmetry. It is the

only spin-allowed transition expected in a high d^4 system^{6,17}. A most important feature of its ground state is that, according to the Jahn-Teller theorem, it must cause distortion in the surrounding octahedron and this distortion should be of appreciable magnitude because of the odd number of e_g electrons—one in this case.

The change in the position of the bands maxima might be generally correlated with the ionic radii of the cations. The bands usually shifted to higher wavelengths with the increase in the ionic radius of the cations or the decrease of its polarising power on neighbouring oxygen ligands. This in accordance with the assumptions of F.E. Ilse and H. Hartmann¹⁸ and S. Kumar⁴.

The observed splitting might be due to the presence of two coordination states for the Mn^{3+} ions as observed in the optical absorption of other transition metal ions^{1,4-6}. A further possibility is that distortion of the spinel structure of the Mn_3O_4 in which the Mn^{2+} ions are tetrahedrally coordinated, and the Mn^{3+} ions are in octahedral coordination. Each of the latter sites tends to distort its own octahedron and the cumulative effect is that the entire lattice is distorted from cubic to elongated tetragonal¹⁷. G. Davies and K. Kustin¹⁹, and T.S. Davies *et al*²⁰ attributed the splitting of the band of Mn^{3+} solutions or complexes to tetragonal distortion or to the fact that the cumulative effect of negative charge can indeed cause measurable spectral changes.

The change in the intensities and positions of the bands caused by changing the glass composition, could be attributed to the relative ease with which the various electron transitions within the ionic complexes containing manganese could take place. The screening of the manganese ion would be closest in the cases where the oxygen ions were more polarisable. The change in the molecular extinction coefficient and the magnetic susceptibility when an alkali oxide was replaced by any of the divalent alkaline earth oxides or when boric oxide was replaced by trivalent or tetravalent metal oxides

will presumably depend on: (i) the ability of the oxides of magnesium, zinc and cadmium to form network building units of the type MO_4 groups. Also, their effect could be understood by taking into account their ionic sizes and field strengths. Increasing the amount of MgO , ZnO or CdO in replacement of Na_2O would result in a decrease in the proportion of MO_4 groups, because less oxygen ions would be available and these ions would become enclosed in the interstices; (ii) when replacing soda by lime, strontium or barium oxides, the divalent cations would act as bridges between the structural building units or become enclosed within the structural interstices. Also the interstices formed in the glasses containing these divalent oxides would be larger than the average size necessary to enclose the Na^+ ion, so that the number of interstices would be less. The basicity of these oxides is assumed to be in the order $BaO > SrO > CaO$; (iii) the effect of the trivalent and tetravalent metal oxides will depend on their ability to form MO_4 groups. However, the screening of the tetrahedral groups obtained from alumina would be incomplete due to the residual fields of AlO_4 groups and each tetrahedron would, require a corresponding Na^+ ion in its immediate vicinity.

Magnetic susceptibility: The paramagnetic character of the glasses containing manganese is usually attributed to the presence of five and four unpaired electrons in the divalent and trivalent states of manganese respectively. The experimental magnetic susceptibility of several transition metal ions in glasses, *eg*, Cr^{21} , Co^{22} , $Mn^{3,11,13,23}$, $Fe^{24,25}$ and Ni^{26} were found to vary much more widely with concentration, oxidation-reduction equilibrium, coordination and environment of the transition metal ion.

The change in the environment influences the susceptibility of the multivalent paramagnetic ion through one or more of several means, such as²⁷: (i) shifting the oxidation-reduction equilibrium of the paramagnetic ion; (ii) creation of inhomogeneous electric fields around the paramagnetic ion to cause splitting of multiplet

levels and consequent redistribution of the magnetic susceptibility; (iii) alteration of the coordination number of the paramagnetic ion; and (iv) alteration of the ionic character of the system.

Summary

Optical absorption and magnetic susceptibility of a number of ternary borate glasses containing manganese were carried out.

The results revealed that manganese existed in two different states; divalent manganese ions coordinated with tetrahedral oxygen, and trivalent manganese ions octahedrally coordinated with oxygen. The absorption was a broad band at about 470-520 m μ which sometimes splitted to two or three peaks with high values of molecular extinction coefficient.

The paramagnetic character of the glasses containing manganese ions was attributed to the presence of five and four unpaired electrons in the divalent and trivalent states of manganese respectively. The ratio of trivalent to divalent manganese ions depended on several factors, including the polarisability of the oxygen ligands surrounding the manganese ions, the presence of bridging and non-bridging oxygen ions, the basicity and acidity of the base glass, and the ability of some of the divalent, trivalent and tetravalent metal oxides to form network-forming units in the glass structure.

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INFRARED STUDIES OF SOME JAMMU CLAYS

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Introduction

In the past two decades, it has been increasingly realised that IR spectrum is a molecular 'finger print' and the technique can be effectively used not only to identify organic compounds but also minerals present in clays.

Basically, IR spectrum comprises the portion of the electromagnetic spectrum lying between the long wavelength edge of the visible and the short end of radio microwave spectrum. One can conveniently divide the IR region in two parts; the near infrared from 0.75 to 25 micron and far infrared from 25 to 1000 micron. The spectra in the former are obtained from the resonance absorption of monochromatic radiations of wavelength corresponding to the vibrational frequencies of specific atoms or group of atoms involved in changing the dipole moment of the molecules; whereas, the absorption of radiations in the region from 25 to 1000 micron reflects the presence of complex molecular rotational or massive lattice vibrational energy levels. It is the spectrum which lies between 2 to 16 micron which is of interest for most of the clay mineral molecules.

A number of authors have utilised IR technique both in India¹⁻³ and abroad⁴⁻¹⁰ to identify clay minerals, study their structure and evaluate physico-chemical properties.

In the present paper, IR analysis of six clays using Nujol as mulling agent, have been presented. An attempt has also been made to correlate and supplement the results with other analytical techniques employed¹¹⁻¹⁴ for the identification of mineral constituents of these clays.

Observations and discussions

The absorption spectra of the clays (cl-1 to cl-6) are given in Fig 1. The position of absorption peaks and band centres with their relative intensity, as estimated visually, is recorded in Table I.

It was observed that between 2.8 micron, all spectrograms showed absorption peaks located at about 2.85, 3.05, 3.50, 4.30, 6.10, 6.80 and 7.20 micron and a broad band of varying width at 8-10 micron. Cl-6 gave an intense doublet at about 12.35 and 12.70 micron. All other clays gave moderate to weak absorption peaks between 10 and 14 micron before showing a gradual increase in the transmission towards longer wavelengths.

With the exception of cl-6, the absorption feature of all other clays were similar, indicating the presence of some common mineral constituents in them.

Although the individual assignment of the bands in clays, with different atomic groupings, is yet not well decided, it is believed¹⁵⁻¹⁶ that the absorption bands at about 2.85 micron is due to hydroxyl groups in the structure, *ie*, unbonded or free hydroxyls. While, the absorption at 3.05 micron may be ascribed to hydrogen bonded hydroxyls, the band at 6.1 micron represents adsorbed water.

Bands centred at 3.50, 6.80 and 7.20 micron appear¹⁷ due to the presence of Nujol used as mulling agent and, therefore, are not diagnostic of any mineral.

The position of the peaks in spectrograms of cl-1 to cl-5 indicated that while cl-1 contained only montmorillonite, cl-2 to cl-5 showed the presence of montmorillonite and illite both. The absorption maxima at 2.85 and 6.10

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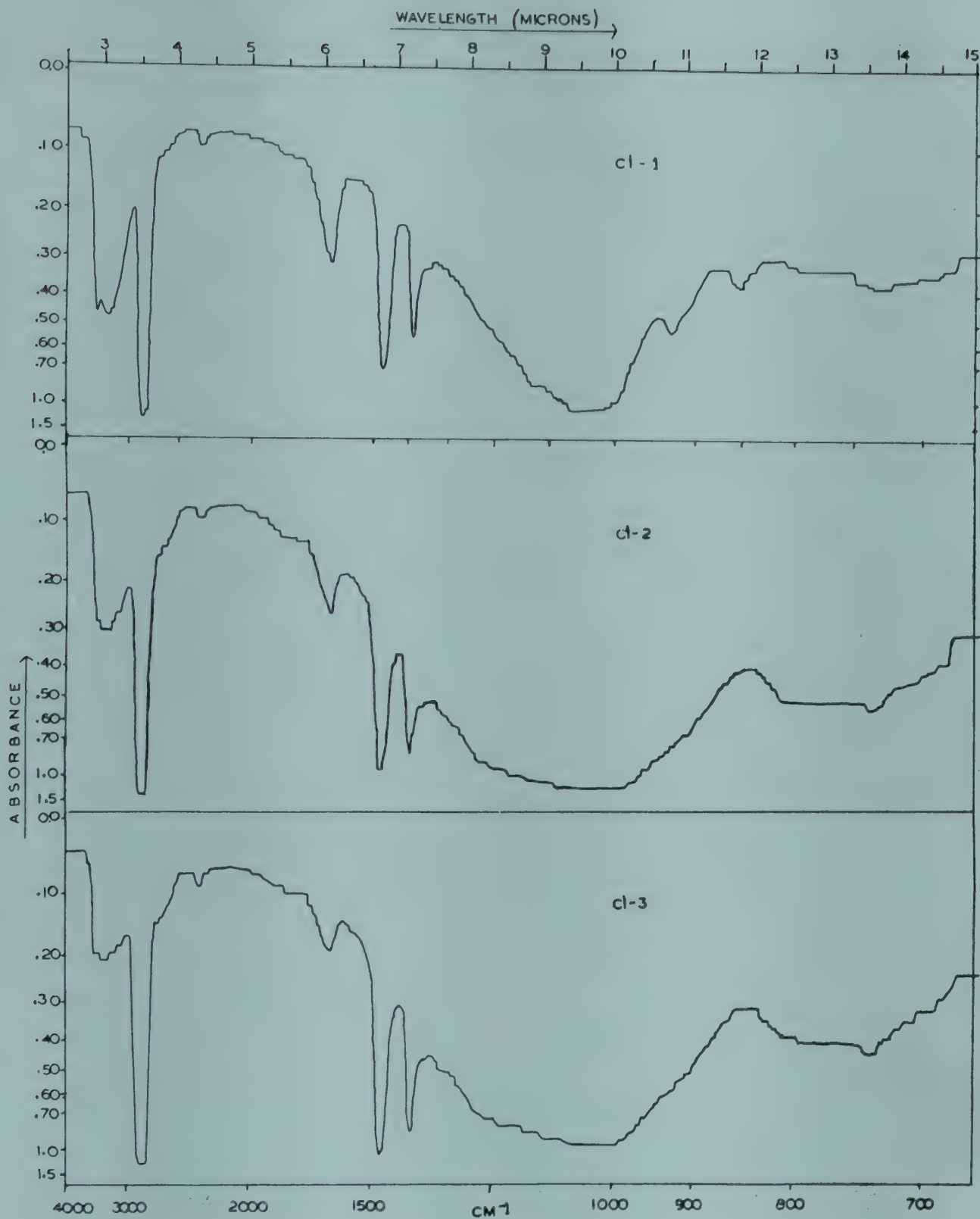


Fig 1(a)
IR spectra of clay samples (unwashed)

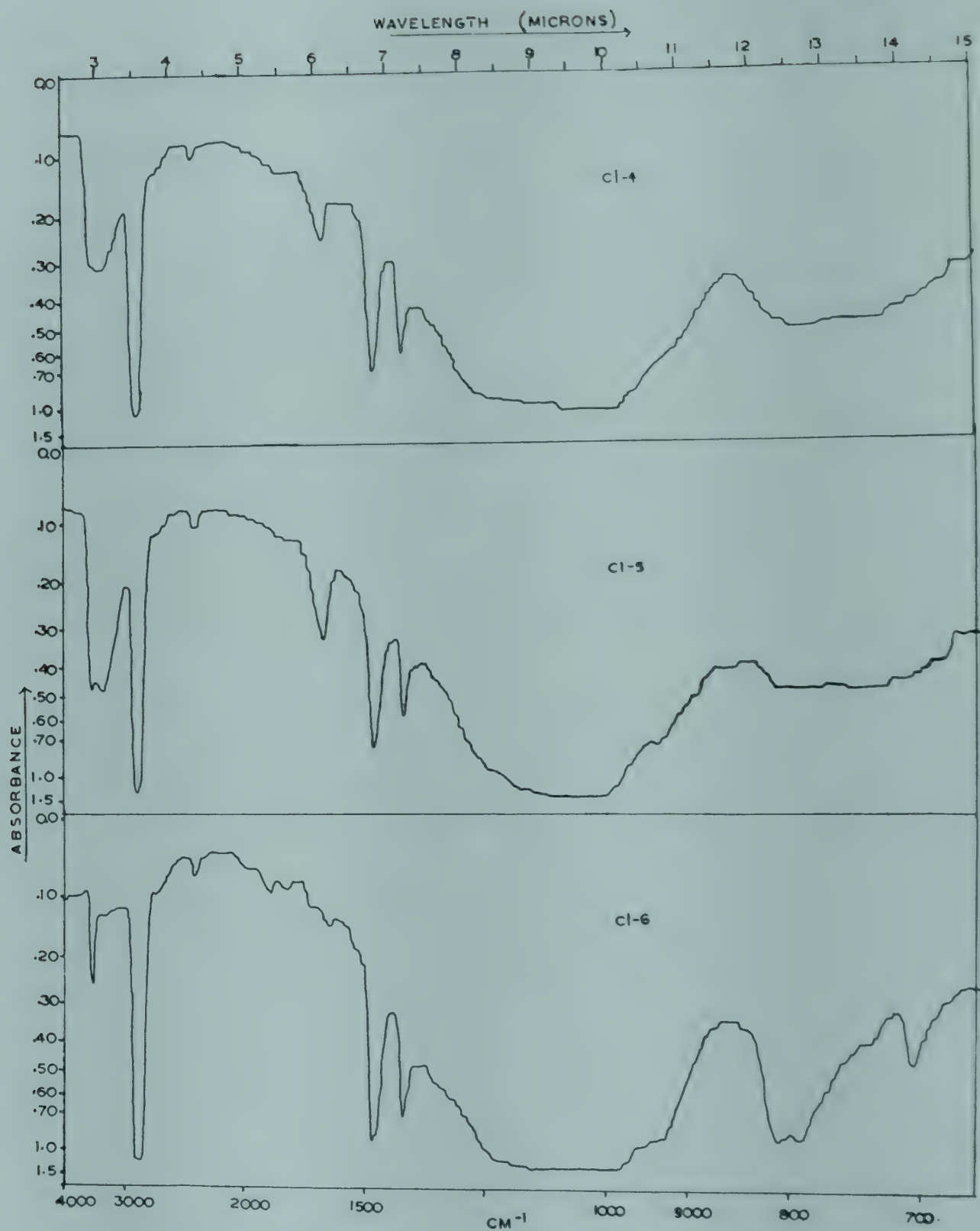


Fig 1(b)
IR spectra of clay samples (unwashed)

TABLE I

The position and intensity of IR absorption peaks for the clays

The position and intensity of absorption peaks between						
Clay number	2-4 micron	4-6 micron	6-8 micron	10-12 micron	12-14 micron	Beyond 14 micron
cl-1	2.85 M 3.05 M 3.55 VS	4.30 VVW	6.10 W 6.80 S 7.20 M	10.85 M 11.75 W		
cl-2	2.85 W 3.10 W 3.50 VS	4.30 VVW	6.10 W 6.80 S 7.15 S	11.05 M	13.50 MB	14.25 W
cl-3	2.90 W 3.05 W 3.50 VS	4.30 VVW	6.05 W 6.75 S 7.20 S	10.90 W	13.60 MB	14.20 W
cl-4	2.90 W 3.05 W 3.50 VS	4.30 VVW	6.05 W 6.75 S 7.20 S 7.65 W	11.00 W		14.15 W
cl-5	2.85 W 3.05 W 3.50 VS	4.30 VVW	6.05 W 6.75 S 7.20 S	10.80 M		14.30 W
cl-6	2.85 W 3.05 VS 3.50 VS	4.30 VVW 5.30 VVW 5.55 VVW	6.15 VW 6.80 S 7.20 S		12.35 S 12.70 S	14.30 M 14.40 W

W—weak, VW—very weak, VVW—very very weak, M—medium, S—strong, VS—very strong, MB—medium band

micron was more pronounced in cl-1 and cl-5 suggesting that these two clays have greater capacity for water absorption than cl-2, cl-3 and cl-4, perhaps owing to the presence of greater montmorillonite content in them. This observation is in conformity^{11,12} with the bec and swelling behaviour of these clays. In cl-6, the amplitude of the absorption peak due to lattice hydroxyl was larger than bounded hydroxyl and it also showed minimum absorption at 6.1 micron.

Although, in montmorillonites, the distinction between absorption peaks due to silica tetrahedra and alumina octahedra, has not been clearly made; yet the number of frequencies have been suggested⁵ for this mineral. Spectra of various silicates, of which clays are representative, have been defined¹⁸ by one main absorption band between 9 and 10 micron, assigned to SiO₄ group. V. Stubicon¹⁰ suggested that Si-O

linkage is represented by the band in the region 8 to 10 micron, whereas, octahedral alumina was represented between 10 and 11 micron. Thus the broad band observed between 8 and 10 micron in all clays represented both tetrahedral Si-O linkage and octahedral alumina.

Although absorption peaks corresponding to montmorillonite and illite lie in the range of 9 to 10 micron, they cannot be easily distinguished¹⁹ because of very narrow difference in the peak positions of the two minerals. In clays under study, these peaks did not appear at all and it was not possible to identify these minerals only on the basis of the absorption between 9 and 10 micron.

Very weak to weak absorption bands were perceptible at longer wavelengths. The distinct bands at 10.85 and 11.75 micron observed in cl-1 were perhaps due to the presence of montmorillonite. Although cl-5 also showed an

absorption peak of moderate intensity at 10.80 micron representing montmorillonite, this peak was of very low intensity in cl-2, cl-3 and cl-4. Here it also shifted towards longer wavelengths. The absorption bands at 13.50 micron in cl-2 and 13.60 micron in cl-3 with moderate intensity corresponded to the presence of illite or kaolinite or both. Although, H. H. Adler⁵ attributed this band to the presence of kaolinite, nontronite, halloysite and illite, the chemical, X-ray and differential thermal analyses¹⁴ of these clays excluded the possibility of the existence of kaolinite or halloysite or nontronite in these samples. A very weak absorption peak observed at 14.20 micron with the exception of cl-1 indicated the presence of illite in them.

Infrared spectrum of cl-6 in the wavelength region of 12 to 13 micron was significantly different from others and it showed an intense and well resolved doublet at 12.35 and 12.70 micron, indicating the presence of quartz. The absorption peak at 14.40 micron in it indicated the presence of kaolinite also. These results are in agreement with those obtained using other analytical techniques¹³.

Thus, the position and relative intensity of observed bands revealed that cl-1 contained only montmorillonite, whereas other clays also contained illite in addition to montmorillonite. Cl-6 was a mixture of quartz, illite and kaolinite.

Although IR spectra of clays which represented particular atomic groupings and their vibrations in particular wavelengths were diagnostics of mineral constituents present in a clay in the

region 2 to 15 micron, yet the literature provided variations in the position, as well as, intensity of the characteristic peaks of various minerals which they represented. The variations observed in the spectral features of clays under investigations, particularly with regard to the position and intensity of their peaks were only marginal and results obtained were compatible with the standard values reported⁵. Such variations might be attributed²⁰ to the presence of varying amounts of constituent minerals in each sample, the difference in their particle size and the degree of crystallinity of individual sample.

Summary

The IR analysis of the six clay samples from Jammu revealed that five of the clays were bentonitic in character. While one clay (cl-1) was only montmorillonite, cl-2 to cl-5 also contained illite in them. Cl-6 was kaolinitic with kaolinite, quartz and illite.

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A LOW SOLUBILITY LEAD-BORACIC GLAZE—PART II

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Introduction

In an earlier paper¹ the development of a low solubility lead boracic glaze using glass cullet of known composition was described. The same glaze was also developed using common glaze raw materials. The firing temperature of the glaze was 1140-1200°. This glaze was further modified to suit delicate underglaze colours like pink and green but in this change its craze resistant property had deteriorated. It is essential for an earthenware glaze to be craze re-

sistant since the earthenware body is quite porous by nature and once the glaze starts crazing the utility of such articles is completely lost. It is thoroughly unhygienic to use a crazed earthenware article for dinnerware purposes.

This paper describes the development of anticraze glaze suitable for delicate underglaze colours like pink and green.

Experimental

The earthenware glaze, earlier developed from glass cullet, had the molecular formula: 0.10 K₂O, 0.078 Na₂O, 0.483 CaO, 0.096 MgO,

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0.076 ZnO, 0.18 PbO, 0.26 Al₂O₃, 0.35 B₂O₃, and 2.8 SiO₂. MgO and ZnO of the glaze was completely replaced by BaO both in the frit and in the mill mixture, while developing delicate underglaze colours. This glaze composition is given in Table I(a) and I(b).

In this glaze (Table I) the colours were found to develop nicely but the glaze was found insufficiently craze resistant.

Increase of BaO to 0.172 mole made the final

glaze low fusing and it showed excessive flowing. It also showed tendency for crazing. The craze resistant property did not improve even when SiO₂ was increased by 0.20 mole. The maturing temperature remained as before. Further modification was made by decreasing BaO to 0.13 mole keeping other ingredients the same in one case and in the second, PbO was decreased to 0.15 mole keeping BaO as 0.096 mole as in the original glaze. The molecular composition of

TABLE I(a)

Mole composition of glazes for delicate pink and green underglaze colours

	K ₂ O	Na ₂ O	CaO	BaO	PbO	Al ₂ O ₃	SiO ₂	B ₂ O ₃
Lead frit	—	—	0.200	—	0.180	0.06	1.00	—
Borax frit	—	0.078	0.133	0.172	—	0.04	0.85	0.35
Mill addition	0.10	—	0.150	—	—	0.16	0.95	—
	0.10	0.078	0.483	0.172	0.180	0.26	2.80	0.35

TABLE I(b)

Batch composition of glazes for delicate pink and green underglaze colours

	Lead frit	Borax frit	Borax	Boric acid	Red lead	Whiting	Barium carbonate	Felspar	Clay	Quartz
Lead frit batch	—	—	—	—	31.78	15.44	—	—	11.97	40.83
Borax frit batch	—	—	18.87	15.27	—	8.43	21.50	—	6.55	29.38
Mill batch	35.00	35.22	—	—	—	4.47	—	16.57	4.61	4.12

TABLE II

Molecular composition of the modified glazes

Glaze	K ₂ O	Na ₂ O	CaO	BaO	PbO	Al ₂ O ₃	SiO ₂	B ₂ O ₃
1	0.100	0.078	0.483	0.130	0.180	0.260	3.00	0.350
2	0.100	0.078	0.483	0.096	0.150	0.260	3.00	0.350 RO=0.907
3*	0.110	0.086	0.532	0.106	0.165	0.286	3.30	0.386

*After making to unity the glaze composition number 2 stands modified as number 3

the two modified glazes are given in Table II.

Lead frit was compounded as lead-bisilicate and CaO and Al_2O_3 were also incorporated in the frit to reduce the solubility of lead. This made the melt slightly high melting. The temperature of smelting was found to be above 1400° and the frit showed good flow while pouring. Borax frit was compounded according to ratio $\text{R}_2\text{O} : \text{RO}_2$ as 1 : 3. The temperature of smelting was about 1360° at which the frit poured well. Lead and borax frits together with the balance materials were ground in porcelain pots for 40 hours using porcelain balls, with 1:1 ratio of material to grinding media, adding 50 per cent water. The ground glaze was found to pass 270 mesh sieve

leaving +0.1 to 0.2 per cent residue on the sieve.

Biscuited crucibles, cups and saucers of a body composition (Table III) were taken as samples for colour experiments. Colour bands were applied on the articles without adding any fluxes and after drying the samples were glazed by hand dipping process. The decorated and glazed samples were fired in electric and oil fired furnaces in 18 hours firing schedule at 1165° (Orton cone 2 down), giving soaking of one hour at peak temperature. Fired samples were examined visually for the flowing of colours. Autoclave crazing test, lead solubility test, hardness test (by indentation method) were carried out.

Chromium oxide base colours such as pink and green got affected by glazes containing ZnO and the colours turned brown owing to reaction between chromium oxide and zinc oxide. Calcium oxide up to certain percentage was observed to increase redness of stain and helped development of colour at lower temperature. High quantity of borax affected red colour in as much as it imparted a lilac tone. When barium oxide was substituted in place of calcium oxide in the glaze the chromium colour developed a darker green. Fairly high CaO in the glaze prevented boric oxide from affecting the green colour. Increase of SiO_2 by 0.20 mole did not make the glaze harder and excessive flowing characteristic of the glaze continued. Decreasing BaO to 0.13 mole the excessive flowing of the glaze was arrested and the colours were bright. On a hard bisque body

TABLE III
Body composition

	Plastic bodies		Casting bodies	
	1	2	3	4
Rajmahal clay	5	3	—	30
Exp china clay	20	22	32	20
Kashimbazar clay	—	—	23	—
Chaibasa clay	14	9	—	—
Saurashtra plastic fire-clay	17	18	—	—
Felspar	13	13	25	13
Quartz	28	32	15	32
Whiting	3	3	3	5
Talc	—	—	2	—

TABLE IV
Batch composition of the final glaze

	Lead frit	Borax frit	Red lead	Felspar	Whiting	Barium carbonate	Borax	Boric acid	Clay	Quartz
Lead frit batch	—	—	27.90	—	16.30	—	—	—	12.60	43.10
Borax frit batch	—	—	—	—	9.30	13.30	20.90	16.90	7.20	32.20
Mill batch	33.67	32.37	—	16.87	4.55	—	—	—	4.70	7.84

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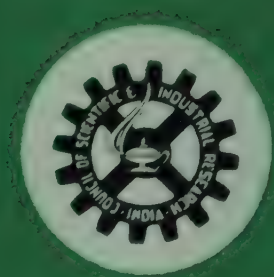
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Vol 24, No 1, 1977

Investigations on cadmium-selenium red stains. N. Roy and S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (1) 1-3 (1977).

The results of investigations on development of cadmium-selenium red stains are presented. Their production procedure and the factors affecting the reproducibility of uniform red colours are also discussed.

Estimation of potassium by potassium ion selective glass electrode. A. P. Bhattacharjee and S. K. Guha, *Cent Glass Ceram Res Inst Bull*, **24** (1) 4-8 (1977).

Silicate samples of different compositions were analysed for their potassium contents by means of a glass electrode. The results obtained are presented in this paper. They are found to be comparable to those obtained by flame spectrophotometry.

Absorption spectra and magnetic properties of some cabal glasses containing manganese. H. A. El-Batal and N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **24** (1) 9-15 (1977).

Paramagnetic susceptibility and molecular extinction coefficient of substituted cabal glasses were studied.

Optical and magnetic properties of $\text{Na}_2\text{O-B}_2\text{O}_3$ glasses. N. A. Ghoneim and H. A. El-Batal, *Cent Glass Ceram Res Inst Bull*, **24** (1) 15-21 (1977).

Absorption spectra and magnetic susceptibility of sodium borate glasses containing manganese were studied. Several reasons have been suggested for splitting of the absorption band due to trivalent manganese ions into two or three peaks.

Permittivity in the microwave region of some silicate and ferrite minerals at low pressures. K. N. Abd-El-Nour, L. G. Girgis and F. F. Hanna, *Cent Glass Ceram Res Inst Bull*, **24** (1) 22-25 (1977).

Dielectric permittivity and attenuation of some silicate and ferrite minerals caused by the inserted sample are increased by increasing the pressure. The results obtained are presented.

Improving the performance of glass melting tank furnaces. U. N. Nayak, *Cent Glass Ceram Res Inst Bull*, **24** (1) 26-30 (1977).

Scope for improving the performance of indigenous glass melting tank furnaces are reviewed. Various aspects of designs to improve efficiency of the furnaces are also discussed.

CENTRAL GLASS AND CERAMIC RESEARCH INSTITUTE BULLETIN

Vol 24, No 1, 1977

Récherches sur les pigments rouges obtenus à partir de cadmium-sélénium. N. Roy et S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (1) 1-3 (1977).

Les auteurs présentent dans cet article les résultats d'une étude sur le développement de pigments rouges obtenus à partir de cadmium-sélénium. Ils discutent aussi de la méthode de leurs productions et des facteurs affectant la reproductibilité des couleurs rouges uniformes.

Détermination de la teneur en potassium au moyen d'électrode sélective de l'ion potassium en verre. A. P. Bhattacharjee et S. K. Guha, *Cent Glass Ceram Res Inst Bull*, **24** (1) 4-8 (1977).

On analyse des échantillons de silicate de compositions différentes pour déterminer la teneur en potassium au moyen d'une électrode en verre sélective pour le dosage du potassium. Les résultats présentés dans cet article sont comparables à ceux obtenus par spectrophotométrie de flamme.

Spectre d'absorption et propriétés magnétiques de quelques verres cabals contenant du manganèse. H. A. El-Batal et N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **24** (1) 9-15 (1977).

On étudie la susceptibilité paramagnétique et le coefficient d'extinction moléculaire des verres cabals substitués.

Propriétés optiques et magnétiques de verres $\text{Na}_2\text{O-B}_2\text{O}_3$. N. A. Ghoneim et H. A. El-Batal, *Cent Glass Ceram Res Inst Bull*, **24** (1) 15-21 (1977).

Les auteurs étudient le spectre d'absorption et la susceptibilité magnétique des verres de borate sodique contenant du manganèse. On donne plusieurs raisons pour la séparation de la bande d'absorption en deux ou entours crochets due aux ions manganèses trivalents.

Permittivité dans la région de micro-onde de quel-

ques minéraux de silicate et de ferrite aux basses pressions. K. N. Abd-El-Nour, L. G. Girgis et F. F. Hanna, *Cent Glass Ceram Res Inst Bull*, **24** (1) 22-25 (1977).

La constante diélectrique et la perte diélectrique de quelques minéraux de silicate et de ferrite, produites par l'échantillon à essayer, s'accroissent par l'augmentation de la pression mécanique. On présente les résultats obtenus.

Amélioration du comportement des fours à bassin pour la fusion du verre. U. N. Nayak, *Cent Glass Ceram Res Inst Bull*, **24**(1) 26-30 (1977).

Dans cet article l'auteur rédige ses pensées sur la possibilité d'amélioration de la productivité des fours à bassin pour la fusion du verre conçus en Inde. Il discute aussi de différents aspects des constructions de four en relation avec la qualité et le rendement de la production.

CENTRAL GLASS AND CERAMIC RESEARCH INSTITUTE BULLETIN

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Untersuchungen an Kadmium-Selenium rote Beizen. N. Roy und S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (1) 1-3 (1977).

Die Ergebnisse der Untersuchungen an die Entwicklung der Kadmium-Selenium roten Beizen sind in der vorliegenden Arbeit dargestellt. Ihr Produktionsverfahren und die Faktoren, die die Reproduzierbarkeit der gleichmässigen roten Farben beeinflussen, sind auch diskutiert.

Abschätzung von Kalium mit Hilfe der Kalium-Ionen-Selektiv-Elektrode. A. P. Bhattacharjee und S. K. Guha, *Cent Glass Ceram Res Inst Bull*, **24** (1) 4-8 (1977).

Silikatproben verschiedener Zusammensetzungen wurde analysiert, um ihre Kaliumgehalts festzustellen, mit einer Glaselektrode. Die erhaltenen Ergebnisse sind in der vorliegenden Arbeit dargestellt. Sie sind vergleichbar mit den Ergebnissen erhalten mittels der Flammenspektralphotometrischen Methode.

Absorptionsstreifen und magnetische Eigenschaften von einigen Manganhaltigen 'Kabal' Gläsern. H. A. El-Batal und N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **24** (1) 9-15 (1977).

Paramagnetische Suszeptibilität und Molekularextinktionskoeffizient von substituierten 'Kabal' Gläsern wurden untersucht.

Optische und magnetische Eigenschaften von $\text{Na}_2\text{O-B}_2\text{O}_3$ Gläsern. N. A. Ghoneim und H. A. El-Batal, *Cent Glass Ceram Res Inst Bull*, **24** (1) 15-21 (1977).

Absorptionsstreifen und magnetische Suszeptibilität von Manganhaltigen $\text{Na}_2\text{O-B}_2\text{O}_3$ Gläsern wurden untersucht. Verschiedene Gründe sind vorgeschlagen für die Aufspaltung der Absorptionsstreifen in zwei oder drei Kurvenscheitelpunkten wegen der dreiwertigen Mangan-Ionen.

Die Dielektrizitätskonstante in der Mikrowellenzone von einigen Silikat- und Ferritmineralien bei niedrigen Drücken. K. N. Abd-El-Nour, L. G. Girgis und F. F. Hanna, *Cent Glass Ceram Res Inst Bull*, **24** (1) 22-25 (1977).

Die Dielektrizitätskonstante und Dämpfung von einigen Silikat- und Ferritmineralien, verursacht durch die eingesetzten Proben, nahmen durch Erhöhung des Druckes zu. Die erhaltenen Ergebnisse sind in der vorliegenden Arbeit dargestellt.

Verbesserung der Leistung von Glasschmelzwannenöfen. U. N. Nayak, *Cent Glass Ceram Res Inst Bull*, **24** (1) 26-30 (1977).

Verbesserungsmöglichkeiten der Leistung von einheimischen Glasschmelzwannenöfen sind in der vorliegenden Arbeit zusammengefasst. Verschiedene Aufbau-Aspekte zur Verbesserung der Leistungsfähigkeit sind auch diskutiert.

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INVESTIGATIONS ON CADMIUM-SELENIUM RED STAINS

N. ROY AND S. S. VERMA*

Introduction

Ceramic stains constitute a specialised field of ceramics. The stains are prepared by calcining a mixture of oxides or salts of metals together with certain diluents or modifying agents, followed by washing and fine milling. During calcination, colours are developed and stabilised. The ceramic stains are mixed with suitable frits (vitrifiable materials) and the resulting ceramic/enamel colours are used for decoration and colouring effects on pottery, enamel and glass articles. Important ceramic stains and colours and a number of additional compositions had been developed earlier^{1,2} at the Institute. They are standardised and their optimum working conditions for large scale manufacture have been established.

The paper deals with the red and allied shades of ceramic stains which were not discussed in the earlier communications^{1,2}. These stains form a very important class for reasons, *viz*, the attractive colour appeal and different nature of their compositions³. They primarily comprise cadmium-sulpho-selenide compounds while the other ceramic stains are based on metallic oxides.

Literature review

Cadmium-selenium red stain: Different methods have been described for production of this stain. Red shade is developed by heating cadmium sulphide or cadmium carbonate with sulphur and selenium metal powder within 470°-650°, which increases with selenium contents⁴. Other

methods require: (a) the use of cadmium oxide along with cadmium sulphide, selenium and sulphur⁵; (b) heating cadmium sulphide and selenium in presence of a sulphur absorbing material⁶; (c) calcining cadmium thioselenide and cadmium oxide⁷; (d) forming a mixed crystal of cadmium sulphide and cadmium selenide by heating^{8,9} a mixture of cadmium carbonate, selenium and sulphur in the ratio 6:1:2 at 550°. In general, the basic reaction involved in the formation of cadmium-sulpho-selenide under the calcination conditions used for red stains are the reduction of the starting cadmium compounds (*eg*, CdCO_3 , CdO , CdS) to elemental cadmium in the presence of sulphur and then the final formation of a complex molecule represented by $n\text{CdS}.\text{CdSe}$. The variation in the colour shades from orange red to dark red being effected by varying the CdSe mole content from the range 0.1-0.15 to 1.0-1.5 per CdS mole¹⁰. Preparation of cadmium sulphides and selenides has also been reported from salts of alkali and alkaline earth by coprecipitation and subsequent calcination or by mixing cadmium sulphide and cadmium selenides and subsequent calcination¹¹. In another method, the common discolouration defect of the red stains during application was sought to be eliminated by addition of 2 per cent ammonium vanadate as a stabilising agent during calcination¹².

Experimental

In view of the very sensitive nature of the cadmium-selenium red stains and the difficulties encountered in achieving reproducibility

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from batch to batch, all variable factors involved were closely studied at every stage. The results of this study are discussed below.

Raw materials: Apart from the importance of the purity of the raw materials, their degree of fineness was found to greatly influence the intimate contact between different components which is essential for the chemical and physical reactions occurring during the calcination process for producing uniformly red stains.

Batch mixing: Tested and purified raw materials were mixed intimately either by sieving the mixture through fine mesh sieve or by using a mechanical mixer. Alternately, satisfactory mixing was obtained by prolonged wet grinding of the raw batch in a ball mill to the desired fineness, followed by drying and pulverising the dry mixture before calcination.

Chemical methods, such as coprecipitation of the metallic hydroxides have definite advantages to yield a very homogeneous mixture. These were, however, not tried due to their limitations of high cost of production.

Calcination: The calcination or firing of the raw batch was the most important step as the chemical reactions occurred in solid state during calcination which determined the shade of the colour produced. Any variation in calcination condition was directly reflected in a variation in shade of the red colour. Hence, all

precautions were taken to ensure uniformity of heat-treatment for the successive batches of production. The best method was found to be heating a stainless steel bowl to a red hot condition over a ring burner, charging the batch into the bowl and then baking the mixture with constant stirring until the evolution of fumes was completed. The temperature and time schedule during the baking operation required careful control to avoid volatilisation of selenium and decomposition of the resulting compound. The mixed crystals CdS.CdSe which formed in this calcination were stable up to 650°-800° only. When ammonium nitrate was used in place of sulphur, it was preferable to calcine the batch at a lower temperature of about 600° in a covered basin with suitable outlet for the gases evolved during the process, which takes somewhat longer time.

Washing: It was found necessary to wash the calcined mass either with hot water or with one per cent HCl solution to render it free from all possible traces of soluble salts and impurities.

Grinding: Wet grinding was carried out in a porcelain lined ball mill or porcelain jar to avoid any contamination. The most suitable working conditions for milling were found to exist when equal quantities of porcelain balls and mill charge were used with water content equal to half the weight of the mill charge. The

TABLE I

Batch composition for red stains

Batch number	Raw materials					Colour
	Cadmium sulphide	Selenium metal powder	Precipitated sulphur	Ammonium nitrate	Potassium nitrate	
I	74.4	16.5	9.1	—	—	Bright red
II	74.4	16.5	—	9.1	—	Bright red
III	73.8	17.1	9.1	—	—	Blood red
IV	73.8	17.1	—	9.1	—	Blood red
V	72.4	18.5	9.1	—	—	Dark red
VI	75.0	19.2	—	4.8	1.0	Dark red

milling fineness should be of the order of—300 mesh.

Iron removing: The red stains sometimes pick up traces of iron from the calcining or milling equipment. This should be removed from the red stains by passing the stains over a magnetic separator after washing or after wet milling.

The milled stain is finally dried free from moisture at about 110°, sieved through 100 mesh before packing and storage.

Compositions of red stains

The cadmium-selenium red stains cover a wide range of shades from orange red to bright red and dark red. The pigmentary effect of all these red stains was obtained basically from a cadmium-sulpho-selenide complex. The range of colour varied from orange red to dark red with the progressive introduction of the selenide radical in the cadmium-sulphur complex. The raw materials commonly used for making these stains were cadmium sulphide, selenium metal powder, precipitated sulphur, ammonium nitrate and potassium nitrate (Table I).

Production problems

Reproducibility of uniform colour from batch to batch was the most important problem in the

production of the red stains, for which the following precautions were found necessary.

Raw materials: Each consignment of the raw materials should be checked by chemical analysis or in the form of a small test batch of red stain. The fineness and quality of the raw materials should be uniformly maintained either at the procurement stage or later by purification.

Calcination: The quantity of the raw batch, temperature and schedule of calcination should be maintained closely in each batch.

Washing: Removal of soluble salts and impurities, eg, iron is very important for achieving uniformity of colour in the stains.

Summary

Investigations were carried out to optimise the manufacturing conditions of the cadmium-selenium red stains.

Some of the best compositions for producing bright to dark red stain and different production problems for producing uniform shades of red stains have been discussed.

Acknowledgment

The authors thank Shri K. D. Sharma, Director of the Institute, for his kind permission to publish this paper.

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ESTIMATION OF POTASSIUM BY POTASSIUM ION SELECTIVE GLASS ELECTRODE

A. P. BHATTACHARJEE AND S. K. GUHA*

Introduction

Since the development of H^+ ion sensitive glass electrode, extensive work¹⁻¹⁰ has been carried out for the development of suitable glass compositions for electrodes which would respond selectively to cations, like sodium and potassium.

At CGCRI, glass electrodes have been developed for selective determination of K^+ ions. Results of measurements of potassium in silicate samples by K^+ selective glass electrodes are presented in this communication.

Experimental

Good electrodes were fabricated from types K_1 and K_3 potassium ion selective glass compositions by blowing bulbs at the end of lead glass tubings matching well with the thermal expansion of the electrode glasses. Ag/AgCl electrode was used internally within the glass electrodes having buffered chloride solution within the bulbs. Hg/Hg₂Cl₂, KCl electrode was used as reference electrode during pK and dc resistance measurements.

DC resistance of the glass electrodes was measured by means of a dc microvoltmeter with 100 megohms internal resistance. One Vibret pH meter model 3920 having accuracy of 0.005 was used for pK (inverse logarithm of K^+ concentration) measurements after standardisation of the pH scales of the instrument as pK scales, with standard KCl solutions of known pK values.

During pK measurements, one jet tipped U

shaped agar/KCl conducting bridge was used for electrolytic connections between the K^+ ion and the calomel reference electrodes dipped in test solution and saturated KCl solutions respectively in order to avoid the leaching of KCl to the test solution from the calomel electrode.

Standard KCl solutions of different strengths as also standard NaCl, CaCl₂, MgCl₂, FeCl₃, AlCl₃, Ba(OH)₂ solutions of known strengths were prepared from AR or GR quality reagents and preserved in polyethylene bottles for pK measurements in pure as well as in mixed cation systems. K^+ specificity of K^+ ion electrodes in pure as well as in mixed solutions and consequent interference of foreign ions were studied after standardisation of the electrode each time with a standard KCl solution of known pK value.

In order to combat the interference of Fe^{3+} and Al^{3+} ions on the K^+ ion specificity of these electrodes, Ba(OH)₂ was used successfully in precipitating out those ions. Triethanolamine, the well known chelating agent did not prove quite effective in precipitating out Fe^{3+} and Al^{3+} ions.

A method of preparation of the test solutions from silicate samples was standardised for estimation of potash contents by K^+ ion electrodes. The method comprised weighing out 0.3 gm of the dried and agated sample. It is then digested twice in a platinum dish with HClO₄ and HF on a sandbath. Complete dryness was ensured by baking at low heat for half an hour. Then on cooling, double distilled water was added first with stirring and then one drop of AR HCl was added to it and heated at a low

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temperature for a few minutes when most of the insoluble Al_2O_3 and Fe_2O_3 thus precipitated were filtered and the filtrate was diluted to 100 cc in a volumetric flask. 25 cc of this stock solution was pipetted in a 50 cc volumetric flask along with 5 to 10 cc of N/100 KCl in order to increase the proportion of K^+ than Na^+ in the test solution to which a few drops of methyl red and then $\text{Ba}(\text{OH})_2$ solution were added dropwise till the disappearance of the pink colour of the solution even after heating for half an hour in water bath. The pH of this solution was adjusted at 5.7 ± 0.3 with addition of dil HCl, if necessary. A blank solution was similarly prepared. pK measurements of the test solution as well as of the blank solution were taken by means of K^+ selective electrode and the latter reading was subtracted from the former when the ppm K^+ was calculated for determining the K_2O per cent of the sample as shown in the following example,

$$\text{pK } 2.520 = \frac{N}{\text{Antilog of } 2.52}$$

$$\frac{39.1 \times 10^3}{331.13} \text{ ppm } \text{K}^+ = 118.08 \text{ ppm } \text{K}^+.$$

TABLE I

Comparison of pK values measured by K^+ electrodes in pure KCl solutions with corresponding theoretical pK values

Standard KCl solutions	Theoretical pK values	pK values measured by K^+ ion electrode (with dc resistance in megohms at 27°)			
		$\text{K}_3/7$ (5)	$\text{K}_3/3$ (20)	$\text{K}_1/1$ (25)	$\text{K}_1/3$ (40)
N/10	1.00	1.08	1.05	1.09	1.05
N/20	1.30	1.33	1.33	1.39	1.36
N/50	1.70	1.72	1.72	1.76	1.75
N/100	2.00	2.00*	2.00*	2.00*	2.00*
N/500	2.70	2.69	2.695	2.69	2.71
N/1000	3.00	2.99	3.00	2.92	2.93

*Standardisation value

TABLE II

Interference from 40 ppm Ca^{2+} on pK values measured by K^+ electrodes

Standard KCl solutions	Theoretical pK values	pK values measured by K^+ ion electrodes			
		$\text{K}_3/7$	$\text{K}_3/3$	$\text{K}_1/1$	$\text{K}_1/5$
N/50	1.70	1.70	1.69	1.70	1.71
N/100	2.00	2.00*	2.00*	2.00*	2.00*
N/150	2.70	2.69	2.69	2.67	2.65
N/1000	3.00	3.00	2.99	2.96	2.98

*Standardisation value

TABLE III

Interference from 40 ppm Mg^{2+} on pK values measured by K^+ electrode

Standard KCl solutions	Theoretical pK values	pK values measured by K^+ ion electrodes			
		$\text{K}_3/3$	$\text{K}_3/6$	$\text{K}_1/1$	$\text{K}_1/5$
N/50	1.70	1.70	1.70*	1.70*	1.69
N/100	2.00	2.00*	2.00	2.00	2.00*
N/500	2.70	2.69	2.70	2.69	2.68
N/1000	3.00	2.99	2.99	2.95	2.96

*Standardisation value with K^+ ion electrode

Quite a few silicate samples including glass and feldspar samples from National Bureau of Standards (NBS), USA were analysed for estimating their K_2O content by the above method and the results were compared with those determined by flame spectrophotometry.

Results and discussions

Table I shows that pK readings taken by K_3 type electrodes are more close to the theoretical values in the range of 2.00 to 3.00 pK in pure KCl system than the pK readings by K_1 type electrodes. DC resistance of the K_3 type electrodes are lower than that of the K_1 type.

Interference of Ca^{2+} and Mg^{2+} ions were insignificant in case of K_3 type electrodes whereas some deviations were found with K_1 type electrodes as shown in Tables II and III.

TABLE IV

Interference from Na⁺ on pK values measured by K⁺ electrodes

Standard solution of KCl+NaCl		Theoretical pK values	pK values measured by K ⁺ ion electrodes					
			K ₃ /2	K ₃ /0	K ₃ /0	K ₃ /0	K ₃ /0	K ₃ /0
N/100	Nil	2.00	2.00*	2.00*	2.00*	2.00*	2.02	—
N/100	N/100	2.00	—	1.95	1.955	1.955	1.97	—
N/100	N/200	2.00	—	—	—	1.97	2.00*	—
N/100	N/500	2.00	2.00	—	—	—	—	—
N/50	N/50	1.70	—	1.66	1.685	—	—	—
N/50	N/100	1.70	1.695	—	—	1.69	1.71	—
N/250	N/500	2.40	—	—	—	2.37	2.395	—
N/500	N/100	2.70	—	2.64	2.65	—	—	—
N/500	N/1000	2.70	—	—	—	2.685	2.70	2.70*
N/1000	N/1000	3.00	2.97	—	2.955	—	—	—
N/1000	N/2000	3.00	—	—	—	—	—	3.00

*Standardisation value with K⁺ ion electrode

TABLE V

Interference of Fe³⁺ and Al³⁺ on pK measurements by K⁺ electrodes and effect of triethanolamine as an inhibitor

Standard KCl solutions:		Theoretical pK values	pK values measured by K ⁺ ion electrodes			
(i) with 40 ppm Fe ³⁺ ion			K ₃ /7		K _s /2	
(ii) with 200 ppm Al ³⁺ ion			after TEA addition†		after TEA addition†	
N/50 (I)		1.70	(I) 1.72	1.75	—	—
N/50 (II)		1.70	(II) 1.70	1.70	(II) 1.70	1.72
N/100 (I)		2.00	(I) 2.00*	2.04	(I) 2.00*	2.00
N/100 (II)		2.00	(II) 2.00*	2.00	(II) 2.00*	2.00
N/500 (I)		2.70	(I) 2.58	2.73	(I) 2.32	2.68
N/500 (II)		2.70	(II) 2.68	2.69	(II) 2.68	2.73
N/1000(I)		3.00	(I) 2.70	3.03	(I) 2.42	2.98
N/1000(II)		3.00	(II) 2.96	3.00	(II) 2.96	2.99

*Standard deviation = 0.02

*Standardisation value with K⁺ ion electrode

†After addition of chelating agent triethanolamine to the test solutions

TABLE VI

Effect of pH on pK values measured by K⁺ electrodes

Standard KCl solutions	Theoretical pK values	pK values measured by K ⁺ ion electrode at pH values (obtained with different additions)						
		3.34	3.68	6.09	9.80	10.03	10.30	11.13
N/100	2.00	—	—	2.00*	—	—	—	—
N/500	2.70	2.10	2.28	2.70	2.73	2.735	2.74	2.76

*Standardisations always done at 2.00 pK at pH 6.0

For the next series of experiments, only K₃ type electrodes were employed. Interference of Na⁺ was prominent when present in equal or higher proportion than K⁺ ion contents of the test solutions as shown in Table IV.

Table V shows significant interferences of Fe³⁺ and Al³⁺ ions on the K⁺ ion electrodes. Addition of the chelating agent, *eg*, triethanolamine to the test solution was not much effective in inhibiting the interferences.

The electrode was, however, found to be sensitive to H⁺ ion beyond a certain range. The significance of pH of the test solution by addition of HCl or triethanolamine or Ba(OH)₂ on pK readings was evident from Table VI which showed that lower the pH, lower the pK readings and higher the pH, higher the pK readings though the changes was not strictly proportional. For best pK readings the pH of the test solutions were controlled at about pH 6.0.

From Table VII, the reproducibility and accuracy of K₃ type electrodes in the estimation of K⁺ ion activities in various silicate samples including samples from National Bureau of Standards, USA, have been shown in the comparative data as obtained by the two methods of K⁺ estimation, *viz*, flame spectrophotometry and K⁺ sensitive glass electrode method. The maximum deviation from standard NBS results was found to be 0.199 per cent K₂O (per cent potash). This may be tolerated in standard routine analysis.

For accuracy, the pK readings should be confined within 2.50 to 2.80 pK, by adjustment of dilution of the test solution and of addition

TABLE VII

Comparison of the results of K⁺ determination by K⁺ electrodes and by flame spectrophotometry

Samples	K ₂ O(%) estimation by		Difference in results by the two methods (%)
	K ⁺ ion electrode	flame spectrophotometry	
NBS Na feldspar 99A	5.277	5.23*	+0.047
NBS K feldspar 70A	11.910	11.77*	+0.14
NBS glass 89 (Pb-Ba glass)	8.599	8.40*	+0.199
Mihijam feldspar	12.38	12.20	+0.18
Optical glass DF 623	4.28	4.26	+0.02
HC 519	5.39	5.37	+0.02
BSC 510	14.41	14.03	+0.37
EDF 651	6.115	6.10	+0.015
BF 584	9.19	9.17	+0.02
MBC 572	7.33	7.30	+0.03

*Results from National Bureau of Standards, USA

of extra known KCl solution; because in lower pK readings a difference of 0.005 pK introduced an error of several ppm K⁺ due to logarithmic nature of the pK calculation results. In higher pK readings, KCl diffusion from calomel electrode resulted in an error, if not controlled by agar bridge carefully.

Conclusion

The glass composition K_3 appeared to be more suitable for the measurement of potassium ion activities.

Ca^{2+} , Mg^{2+} ions, as also Ba^{2+} ion exhibited hardly any interfering effect on pK measurements, but Na^+ in higher proportion and Fe^{3+} as well as Al^{3+} ions had significant interference on K^+ ion electrodes. Triethanolamine was not effective in inhibiting completely those interferences.

Potash estimation of silicate samples was made feasible with K_3 type of K^+ ion electrodes by following a chemical technique of preparing the test solutions for pK measurements. The results were quite comparable to those obtained by flame spectrophotometry.

The applicability of the K^+ ion electrodes in potash estimation of silicate samples in a simple way has been estimated from the present investigation and may, therefore, prove to be potentially useful in various fields like agriculture, biochemistry, drugs and foods, fertiliser, oceanography and petroleum industries.

Summary

Several glass compositions were studied particularly in relation to their selectivity for potassium ions. DC resistance of the glasses were measured and the K^+ selectivity of the electrodes made therefrom were examined. The effect of ions like Ca^{2+} , Mg^{2+} , Na^+ , Fe^{3+} or Al^{3+} was also critically studied. Cases of interference were eliminated by standardising a chemical technique of preparation of the test solutions for the pK measurements.

Silicate samples were analysed for potassium contents by means of one type of the glass electrodes and the results were found to be quite comparable to those obtained by flame spectrophotometry.

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ABSORPTION SPECTRA AND MAGNETIC PROPERTIES OF SOME CABAL GLASSES CONTAINING MANGANESE

H. A. EL-BATAL AND N. A. GHONEIM*

Introduction

Manganese ions exist in glasses in two different states¹⁻⁴; divalent faint manganese ions coordinated tetrahedrally with oxygen with very weak bands; and trivalent purple manganese ions octahedrally coordinated with oxygen possessing a broad band with maximum around 470-520 m μ which shows splitting to two or three component peaks.

The energy transition of the spin-allowed Mn³⁺ absorption band²⁻⁶ is $5\bar{3} \rightarrow 5\bar{5}$. A most important feature of its ground state is that according to the Jahn-Teller theorem, it must cause distortion in the surrounding octahedra and this distortion should be of appreciable magnitude because of the odd number of e_g electrons — one in this case.

Optical absorption and paramagnetic susceptibility of some substituted cabal glasses of varied compositions with the aim of studying the Mn²⁺—Mn³⁺ equilibrium in these glasses is reported in this paper.

Experimental

Batch material: The batch materials used were of the chemically pure grade. Boric oxide was introduced as boric acid. Calcium oxide, strontium oxide and cadmium oxide were introduced as carbonates. Alumina was introduced as such. Manganese was added as chemically pure MnO₂.

The batches were all melted in platinum 2 per cent rhodium crucibles in electrically heated

muffle furnaces under normal atmospheric conditions. The temperature of melting was 1350°. The amount of glass melted was 100 gm each melt. Melting was usually continued for four hours. To ensure homogeneity, the crucibles containing the melt was removed from the furnace at intervals and swirled about to promote mixing.

Preparation of test specimens: For the transmission measurements, the glasses were cast into rectangular moulds of about 1 cm² cross-section and 4 cm length. For the magnetic susceptibility measurements, specimen rods were cast of about 10 cm length and 1 cm² cross-section. Grinding and polishing were carried out with the minimum amount of water, and in the final stages of polishing, paraffin oil was used.

The transmission measurements were carried out in the visible and near infra-red region of the spectrum using Beckman DR spectrophotometer. The results were plotted as the molecular extinction coefficient, E_M, against the wavelength. E_M was calculated³ from equation (1):

$$E_M = \frac{OD}{ML} \quad \dots (1)$$

where OD is the optical density at the particular wavelength of a sample of thickness L cm and M the concentration of the transition metal ion in mole/1000 cm³ of the glass.

The magnetic susceptibility of the manganese ions in glass was determined by the Gouy method using the coloured and the corresponding blank glass. The susceptibility was measured

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at field strength of approximately 12,000 gauss. The volume susceptibility was calculated from equation (2):

$$\delta_s = \frac{1}{2}(K_s - K_0) A (H^2 - H_0^2) \\ = \frac{1}{2}(K_s - K_0) \frac{S}{l\sigma_0} (H^2 - H_0^2) \quad \dots (2)$$

where δ_s is the resultant magnetic pull on the specimen; K_s and K_0 the respective susceptibility of the specimen and air; A the cross-sectional area of the specimen; S , σ_0 , l the mass, the density, and the length of the specimen respectively. The mass susceptibility of manganese ions was adjusted to per cent MnO_2 .

Results

Effect of the alkali oxides: The effect of introducing 5, 10 or 20 parts of soda in replacement of lime in the glass of the composition B_2O_3 40, CaO 30 and Al_2O_3 30 per cent containing 0.20 gm MnO_2 per 100 gm glass was studied (Table I). The results obtained are illustrated in Fig 1. The extinction curves obtained showed one broad symmetrical band for each glass with a maximum at 465 nm and a small peak at 430 nm. The molecular extinction coefficients of the main band maxima decreased from 22 to 20.5 and then increased to 21 with the glasses containing 5, 10 or 20 parts soda respectively.

From the results obtained (Table I), it was seen that the paramagnetic susceptibility increased with the increase of the alkali oxide

content, and the order of increase was highest for K_2O followed by soda and lithia.

TABLE I

Composition and magnetic susceptibility of some cabal glasses containing 0.20 gm MnO_2 per 100 gm glass. Each glass was melted for 4 hours at 1350°

Glass	Composition (%)			Mass susceptibility ($\chi \times 10^6$)	
	B ₂ O ₃	CaO	Al ₂ O ₃		
				Na ₂ O	
203	40	25	30	5	0.0880
204	40	20	30	10	0.0953
205	40	10	30	20	0.1032
				K ₂ O	
206	40	25	30	5	0.0906
207	40	20	30	10	0.0993
208	40	10	30	20	0.1075
				Li ₂ O	
209	40	25	30	5	0.0845
210	40	20	30	10	0.0923
211	40	10	30	20	0.1009
				MgO	
212	40	25	30	5	0.0781
213	40	20	30	10	0.0773
214	40	10	30	20	0.0800
				ZnO	
215	40	25	30	5	0.0830
216	40	20	30	10	0.0872
217	40	10	30	20	0.0941
				SrO	
218	40	25	30	5	0.0820
219	40	20	30	10	0.0771
220	40	10	30	20	0.0824
				BaO	
221	40	25	30	5	0.0833
222	40	20	30	10	0.0791
223	40	10	30	20	0.0846
				CdO	
224	40	25	30	5	0.0852
225	40	20	30	10	0.0953
226	40	10	30	20	0.1050

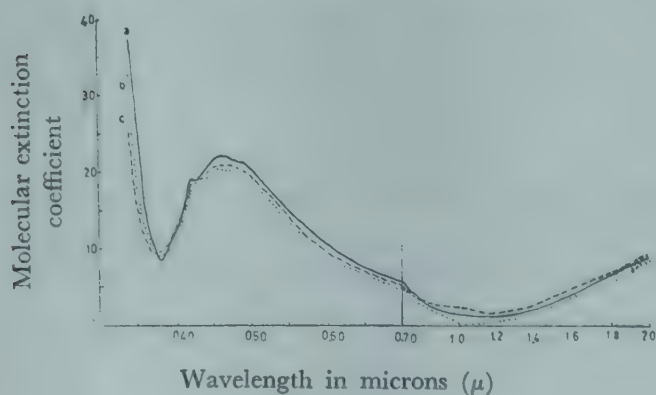


Fig 1

Molecular extinction coefficient of: a-glass 203, b-glass 204, c-glass 205 of Table I

Effect of the divalent metal oxides: The effect of replacing 5, 10 or 20 parts of lime by SrO, BaO or CdO in the glass of the composition B_2O_3 40, CaO 30, Al_2O_3 30 per cent containing 0.20 gm MnO_2 per 100 gm glass was studied (Table I). The results are shown in Figs 2-4.

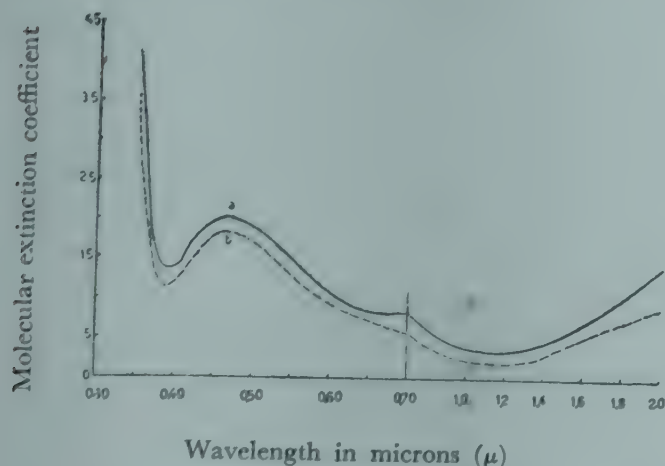


Fig 2
Molecular extinction coefficient of: a-glass 218, b-glass 220 of Table I

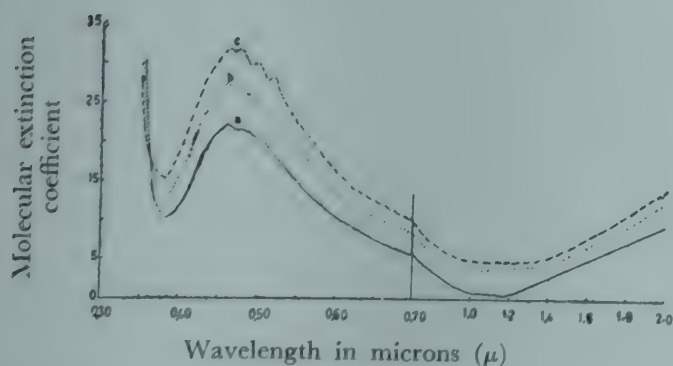


Fig 3
Molecular extinction coefficient of: a-glass 221, b-glass 222, c-glass 223 of Table I

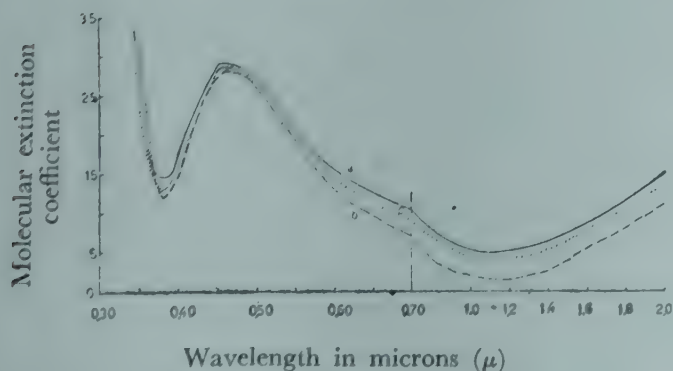


Fig 4
Molecular extinction coefficient of: a-glass 224, b-glass 225, c-glass 226 of Table I

Effect of strontium oxide: The extinction curves showed one broad band with a maximum at 460 nm which tended to resolve into several splitted peaks at 460, 480, 500 and 520 nm, when more of SrO was introduced. The molecular extinction coefficients appreciably increased from 22 with the glass containing 5 parts SrO to 27.5 and 33 for the glasses containing 10 and 20 parts SrO respectively.

Effect of barium oxide: The extinction curves showed one broad symmetrical band with a maximum at 460 nm. The molecular extinction coefficients of the bands maxima slightly decreased from 29 to 28 and then increased to 28.5 with the glasses containing 5, 10 and 20 parts BaO respectively.

Effect of cadmium oxide: The extinction curves showed one broad band with a maximum at 460 nm. The molecular extinction coefficients decreased to 20.5 and 18 with the glasses containing 5 or 10 parts CdO respectively.

From the results obtained (Table I), it was seen that the paramagnetic susceptibility decreased with the first introduction of 5 or 10 parts of MgO , SrO or BaO and then increased with the further addition up to 20 parts. The paramagnetic susceptibility increased progressively with the introduction of ZnO or CdO .

TABLE II

Composition and magnetic susceptibility of some cabal glasses of the composition B_2O_3 40, CaO 30 and Al_2O_3 30 wt per cent containing different amounts of manganese dioxide. Each glass was melted for 4 hours at 1350°

Glass	Composition (%)			MnO_2^* (gm)	Mass sus- ceptibility ($\chi \times 10^6$)
	B_2O_3	CaO	Al_2O_3		
198	40	30	30	0.20	0.0821
199	40	30	30	0.30	0.1253
200	40	30	30	0.75	0.3062
201	40	30	30	1.00	0.4063
202	40	30	30	2.00	0.7801

*per 100 gm glass

Effect of the concentration of the manganese: The paramagnetic susceptibility was found to increase with the increase of the MnO_2 content in the glass (Table II).

Discussions

The 'true' cabal glass contains neither silica nor alkali ions. It consists only of lime, alumina and boric oxide. The oxygen ions donated by the lime, will be largely claimed by the Al^{3+} and B^{3+} ions. The limiting range of glass formation of this type of glass is influenced by the factors⁷: (i) no two AlO_4 tetrahedra can be linked together in any glass, and they should be separated by at least one BO_3 or BO_4 groups. Accordingly the ratio $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ should not be greater than unity. Al_2O_3 in amounts greater than this ratio, can be introduced in the presence of 2.3 mole CaO , probably because Ca^{2+} ions can form bridges between adjacent AlO_4 tetrahedra; (ii) at least one molecule of lime must be present to provide the oxygen required for Al_2O_3 to form AlO_4 tetrahedra; and (iii) the large size of the AlO_4 tetrahedra as compared with the BO_4 tetrahedra or BO_3 triangles would change the general structural features of the borate glasses containing alumina. The holes will be considerably large in volume (as in silicate glasses) and hence big cations could be introduced more easily. With more lime than is required for the tetrahedral coordination of Al_2O_3 , part of the boron ions become tetrahedrally coordinated till one-fifth of the boron ions have formed tetrahedra groups. The excess lime will occupy bridging positions in the network.

A. E. Owen⁸ assumed that all the aluminium and up to one-fifth of the borons might be tetrahedrally coordinated by oxygen ions. But with greater amount of lime than was necessary for this, BO_3 groups with non-bridging oxygen ions were formed and these increased with the increase of the lime content. He concluded that Abe's screening hypothesis⁹ fit quite accurately to the compositional trends observed in the cabal glasses. He further suggested that there were some degree of phase separation, at least

on submicroscopic scale, into a B_2O_3 rich and a $\text{CaO-Al}_2\text{O}_3$ phase.

P. J. Bray *et al*^{10,11} from NMR studies suggested that Abe's hypothesis would be an oversimplification of the structure and that one-fifth of the boron atoms could be tetrahedrally coordinated, and that not all the aluminium become tetrahedrally coordinated with oxygen. They pointed out that in glasses with 1:1 ratio of CaO and Al_2O_3 about 10 per cent of the boron ions were still in four-fold coordination. However, the proportion of non-bridging oxygen ions would certainly be expected to increase with CaO content.

In the base cabal glass investigated, the weight per cent and molecular ratio of the composition B_2O_3 , CaO and Al_2O_3 were 40, 30, 30 and 1.95, 1.82, 1.00 respectively. In this glass, the lime can provide oxygen ions in amounts greater than is required for the tetrahedral coordination of all the aluminium and one-fifth of the boron present. The aluminium will form AlO_4 groups by obtaining the oxygen ions required from 1.0 mole CaO , and only part (0.20 mole CaO) of the excess lime (0.80 mole) would take part in the formation of BO_4 tetrahedra.

Effect of the alkali oxides: The effect of the introduction of the alkali ions for replacement of lime can be explained by considering the mobility effects. The alkali ions occupy holes within the interstices formed by BO_3 , BO_4 and AlO_4 groups. The oxygen ligands are more polarisable in the presence of the alkali ions than with the divalent ions and so can be effective in promoting the presence of trivalent manganese. The difference between the effects of the different alkalies when they are introduced into the cabal glasses may be attributed to the difference in the mobility of the different ions which is governed by the ease of the movement of the atomic aggregates in the glass. The structure of the cabal glasses studied⁷ is similar to the structure of a silicate glass. The structure of the glasses containing potash will, therefore, be more compact than those containing lithia, while the glasses containing soda

will be intermediate. The oxygen ions are more polarisable with potash than with soda, and more with soda than with lithia. As a result, the relative effect of increasing the proportion of the trivalent manganese will be highest for potash followed by soda and least for lithia.

The role of cadmium oxide: The first addition of this oxide brings about the formation of the tetrahedral groups of CdO_4 . A competition for the oxygen of the lime is to be found between: (i) Al_2O_3 to form tetrahedra, (ii) CdO to form CdO_4 group and (iii) B_2O_3 to form BO_4 tetrahedra.

It has been concluded by several authors^{7,8,12} that the Al^{3+} ions assume tetrahedral coordination with oxygen in preference to the boron ions, because this was considered to be the only stable state for the Al^{3+} ions in the glass structure.

In recent publications, the presence of AlO_6 groups was not proved in $\text{K}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ system¹⁶. But in $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ system it was present as a function of alumina concentration¹⁴. Here the alumina was assumed to exist as AlO_6 if present in small critical concentration of 0.25 wt per cent.

The B^{3+} ion could exist as BO_3 triangles and the Cd^{2+} ions may be partly enclosed in the structural interstices or act as bridges between structural units.

However, in the glasses studied, the lime content was more than required for the tetrahedral coordination of all the Al^{3+} ions and one-fifth of the boron ions, so that part of the Cd^{2+} ions could form CdO_4 groups when these ions were first introduced and they may later enter the glass structure as bridge linkages when more of the ions are added. This condition will first lead to the decrease of the proportion of the $\text{Mn}^{3+}/\Sigma\text{Mn}$ in the glass and then it would increase. The same can be assumed for the role of MgO or ZnO .

The role of strontium or barium oxides: The Sr^{2+} or Ba^{2+} ions can either occupy interstices within the network or form bridges between the network forming units. The tetrahedral units of AlO_4 and BO_4 cannot be linked together but

they are separated by BO_3 triangles or a bridge of the type $=\text{Al}-\text{O}^-\dots-\text{O}-\text{B}=, =\text{B}-\text{O}^-\dots-\text{O}-\text{B}=$, or $=\text{B}-\text{O}^-\dots-\text{O}-\text{B}=$. However, in the composition B_2O_3 40, Al_2O_3 30 and CaO 30 per cent, the number of interstices formed by the structural building units (AlO_4 , BO_4 and BO_3 groups) is greater than the number of Ca^{2+} ions present. The effective factor which determines the condition of manganese ions will be the presence of non-bridging oxygen ions beside the polarising effect of the divalent cations on the oxygen ligands. The introduction of cations having relatively weak potential field, with respect to Ca^{2+} ions, like Ba^{2+} or Sr^{2+} leads to highly polarisable oxygen ligands. Also the relative increase of basicity of the glass by replacing the smaller alkaline earth ion by a large one, i.e., ($\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$), will increase the proportion of the $\text{Mn}^{3+}/\Sigma\text{Mn}$.

Attribution of the number and position of the bands and the reasoning of the observed splitting: The change in the position of the bands maxima might be generally correlated with the ionic radii of the cations. The bands usually shifted to higher wavelengths with the increase in the ionic radius of the cations or the decrease of its polarising power on neighbouring oxygen ligands. This is in accordance with the assumptions of F. E. Ilse and H. Hartmann¹⁵ and S. Kumar².

The splitting of the broad band may be due to the distortion of the spinel structure of the Mn_3O_4 in which the Mn^{2+} ions are tetrahedrally coordinated and the Mn^{3+} ions are in octahedral coordination. Each of the latter sites tends to distort its own octahedron and the cumulative effect is that the entire lattice is distorted from cubic to elongated tetragonal¹⁶. The enhanced intensity of the absorption bands indicates larger distortion of the already distorted Mn^{3+} ions. This extra distortion produces more asymmetry and shifts the band maximum further away from the centro-symmetric group and this produces a higher intensity in the d-d band.

Magnetic susceptibility: The paramagnetism introduced into a glass by the incorporation of the transition metal ions arises from the unpaired

electrons of the unfilled 3-d subshell of these metals. The magnetic properties of the transition metal ions change largely with change in colour. This phenomenon can be explained by the different orbital contributions when the colouring ion is in octahedral or tetrahedral coordination with respect to the surrounding oxygen ligands. According to the ligand field theory, the magnetic behaviour of transition metal ions is also connected with their spatial environment.

The paramagnetic character of the glasses containing manganese is usually attributed to the presence of five and four unpaired electrons in the divalent and trivalent states of manganese respectively. The experimental magnetic susceptibility^{17, 18, 6 & 19, 20, 21} of several transition metal ions in glasses, *eg*, Cr, Co, Mn, Fe, Ni were found to vary widely with change in concentration, oxidation-reduction equilibrium, coordination and environment of the transition metal ion.

The change in the environment influences the susceptibility of the multivalent paramagnetic ion through one or more of several means²², such as: (i) shifting the oxidation-reduction

equilibrium of the paramagnetic ion; (ii) creation of inhomogeneous electric fields around the paramagnetic ion to cause splitting of the multiplet levels and consequent redistribution of the magnetic susceptibility; (iii) alteration of the coordination number of the paramagnetic ion; and (iv) alteration of the ionic character of the system.

In the case of manganese ions which can exist in more than one valence state in glass, electron transfer or partial covalence can take place at favoured orbital overlapping. This tendency increases with the increase in the concentration of the manganese ions.

Summary

Optical absorption and magnetic susceptibility studies of a number of cabal glasses containing manganese were carried out. The results obtained revealed the splitting of the broad band due to the Mn^{3+} ions. The paramagnetic character of the glasses containing manganese ions was attributed to the presence of five and four unpaired electrons in the divalent and trivalent states of manganese respectively.

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OPTICAL AND MAGNETIC PROPERTIES OF $Na_2O-B_2O_3$ GLASSES

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Introduction

The characteristics and the optical absorption bands due to the manganese ions in glasses have been investigated by several authors¹⁻¹⁴. The observed broad absorption band due to Mn^{3+} ions is attributed^{5-7,12} to the spin-allowed transition ${}^5|_3 \rightarrow {}^5|_5$. The four weak bands of the Mn^{2+} ions are attributed to the symmetry of the ions; octahedral or tetrahedral coordination^{9,11}. A. Paul and D. Lahiri¹⁰ found that the manganese ions equilibrium shifted more towards the oxidised state when the alkali oxide concentration

in binary borate glasses increased and or when the basicity increased. A. Paul¹² showed that the absorption of trivalent manganese ions in binary alkali borate glasses could be resolved into two or three Gaussian component peaks centred at about $16,000\text{ cm}^{-1}$ (red peak), $20,000-21,000\text{ cm}^{-1}$ (middle peak) and $24,000\text{ cm}^{-1}$ (blue peak). In the two previous publications^{13,14}, the authors have shown a marked splitting of the broad band of Mn^{3+} ions in a series of alkali borate and lead borate glasses.

In the present investigation, optical absorption and magnetic susceptibility of sodium borate glasses containing varied concentration

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of manganese under different conditions of melting have been studied.

Experimental

The glasses were prepared from chemically pure materials. Boric oxide was introduced as boric acid and soda as sodium carbonate. Manganese was added to the batch as MnO_2 . The glasses were melted in platinum-2 per cent rhodium crucibles in electrically heated muffle furnaces under normal atmospheric conditions. 50 gm of glass was melted usually for four hours at 1000° . To ensure acceptable homogeneity, the crucibles containing the melt were removed from the furnace at intervals and swirled about to promote mixing. For the transmission measurements, the glasses were cast into rectangular moulds 1 cm^2 in cross-section and 4 cm length. For magnetic susceptibility, rods were cast about 10 cm length and 1 cm^2 cross-section. Transmission measurements on ground and polished annealed glasses in the visible and near infrared region were made on a Beckman DR spectrophotometer.

The methods of measuring the molecular extinction coefficient E_M , the mass magnetic susceptibility, and the concentration of trivalent manganese are described earlier^{13,14}.

Results

Effect of the concentration of manganese: Increasing amounts of manganese were added to a composition B_2O_3 70, Na_2O 30 wt per cent. Manganese was introduced in three forms, namely, manganese dioxide, manganese sesquioxide, or as potassium permanganate. The results obtained are shown in Table I and illustrated in Figs 1 and 2.

With the increasing manganese content, the paramagnetic susceptibility progressively increased. With very low concentration of manganese ions (0.01 gm MnO_2) the molecular extinction curve showed a split band with three maxima at about 470, 500 and $520 \text{ m}\mu$. Further increase in manganese diminished the resolution of the

band and one nearly symmetrical band was observed.

When the manganese content reached 0.50 gm per 100 gm glass, six small bands were observed with maxima at about 380, 410, 440, 460, 500

TABLE I

Compositions and magnetic susceptibilities of sodium borate glasses of the composition B_2O_3 70, Na_2O 30 wt per cent containing different additions of different types of manganese oxide. Each glass was melted for four hours at 1000°

Glass	Composition (wt per cent)			Mass suscep- tibility ($\chi \times 10^6$)	$\text{Mn}^{3+} \times 100$ ΣMn
	B_2O_3	Na_2O	MnO_2		
1	70	30	0.01	0.1384	37.34
2	70	30	0.02	0.1432	29.00
3	70	30	0.05	0.1525	26.16
4	70	30	0.075	0.1695	24.90
5	70	30	0.10	0.1787	23.40
6	70	30	0.15	0.1824	17.50
7	70	30	0.20	0.1947	14.90
8	70	30	0.25	0.2107	16.70
9	70	30	0.30	0.2248	13.74
10	70	30	0.50	0.3026	9.00
11	70	30	0.75	0.4028	6.772
12	70	30	1.00	0.4720	6.025
13	70	30	1.25	0.5507	
14	70	30	1.50	0.6056	
15	70	30	2.00	0.8145	
16	70	30	Mn_2O_3 0.01		49.19
17	70	30	0.02		40.97
18	70	30	0.05		26.20
19	70	30	0.075		22.01
20	70	30	0.10		24.60
21	70	30	0.20		18.05
22	70	30	0.50		16.051

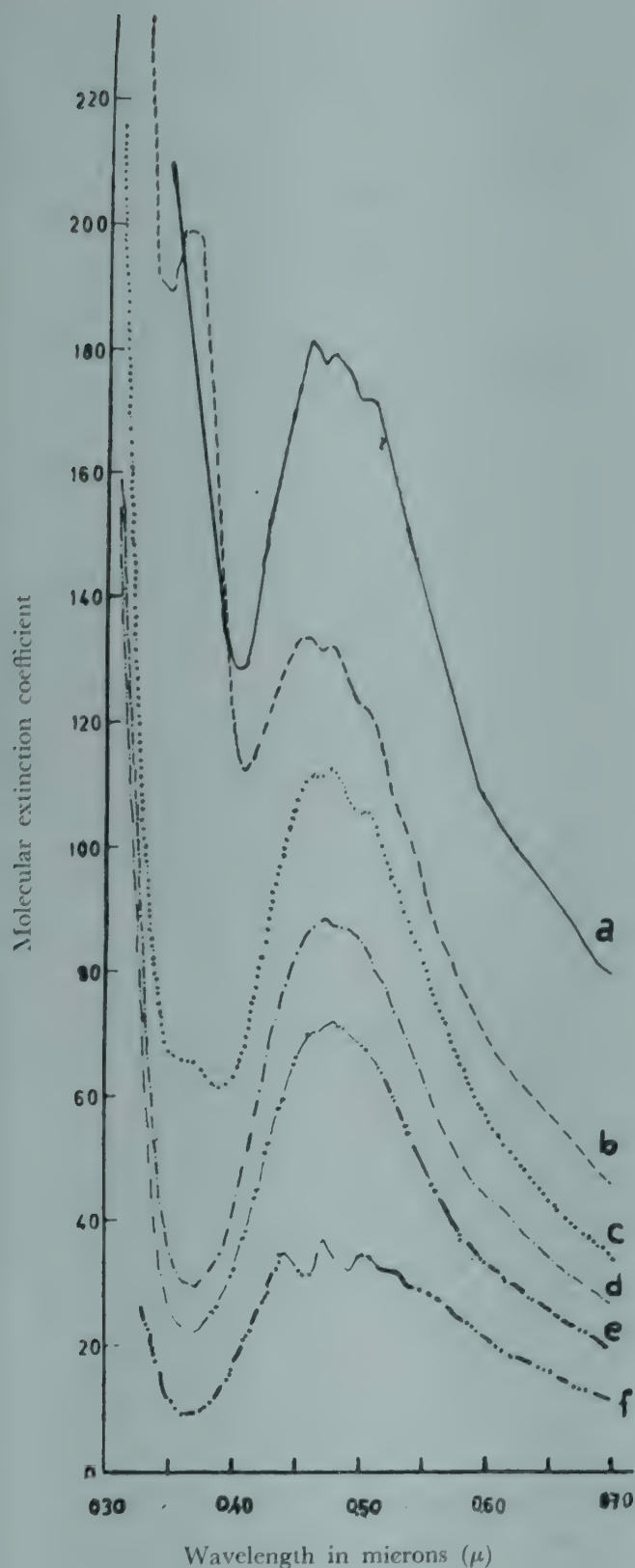


Fig 1

The extinction curves of sodium borate glasses of the composition B_2O_3 70, Na_2O 30 wt per cent containing: (a) glass 17; (b) glass 18; (c) glass 19; (d) glass 20; (e) glass 21; and (f) glass 22

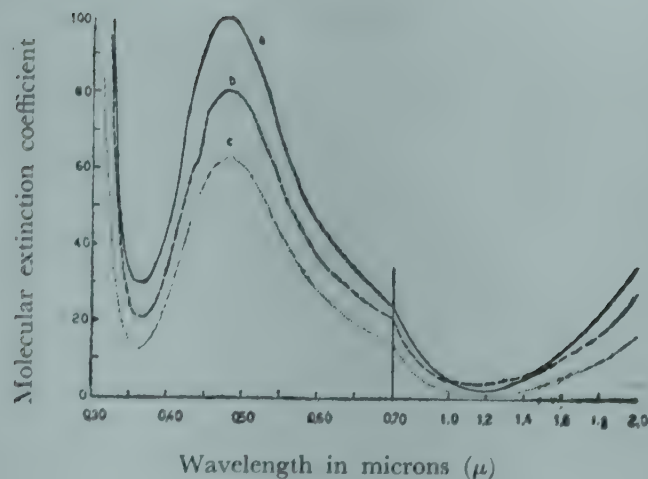


Fig 2

The extinction curves of sodium borate glasses of the composition B_2O_3 70, Na_2O 30 wt per cent containing: (a) $KMnO_4=0.10$ MnO_2 , glass 5; (b) $KMnO_4=0.20$ MnO_2 , glass 7; and (c) $KMnO_4=0.30$ MnO_2 , glass 9

and $540\text{ m}\mu$. The molecular extinction coefficients of the band maxima decreased with the increase of the manganese ions content. The ratio $Mn^{3+}/\Sigma Mn$ progressively decreased with increase of the manganese content.

Effect of temperature of melting: The effect of the temperature of melting on the spectral absorption curves was studied by melting the batch B_2O_3 70, Na_2O 30 wt per cent containing 0.02 gm MnO_2 per 100 gm glass at temperatures ranging from 900° to 1100° as shown in Table II and represented diagrammatically in Fig 3.

The spectral curves for the glasses melted at 900° , showed triple-split bands with peaks around 460, 500 and $530\text{ m}\mu$. When the temperature of melting was increased, the spectral curves showed one broad symmetrical band centred at about $465\text{ m}\mu$. The molecular extinction coefficient of the highest band maxima decreased with the increase of the temperature of melting of the glasses.

Effect of the duration of melting: The effect of the duration of melting on the transmission of glasses containing manganese was carried out by preparing specimens of the glass of the composition B_2O_3 70, Na_2O 30 wt per cent, containing 0.20 gm MnO_2 per 100 gm glass with different melting times ranging from half

TABLE II

Compositions and magnetic susceptibilities of sodium borate glasses of the composition B_2O_3 70, Na_2O 30 wt per cent containing 0.20 gm MnO_2

Glass	Composition (wt per cent)		Time of melting (hours)	Mass suscepti- bility ($\chi \times 10^6$)	$Mn^{3+} \times 100$ ΣMn
	B_2O_3	Na_2O			
23	70	30	$\frac{1}{4}$	0.2172	7.474
24	70	30	$\frac{1}{2}$	0.2044	10.28
25	70	30	1	0.1962	11.21
26	70	30	2	0.1924	12.95
7	70	30	4	0.1947	14.90
27	70	30	6	0.2024	13.08
28	70	30	8	0.2083	12.15
29	70	30	12	0.2065	12.15
30	70	30	24	0.1984	12.15
Temperature of melting (°C)					
31	70	30		900	
7	70	30		1000	
32	70	30		1100	
33	80	20		900	
34	80	20		1000	
35	80	20		1100	

an hour to 24 hours (Table II). The extinction curves are given in Fig 4.

The glass melted for one hour showed peaks at 460, 480 and 510 $m\mu$ and with molecular extinction coefficient of 85, 89 and 87 respectively. As the melting time increased, the splitting disappeared leaving a broad, nearly symmetrical band with its maxima at 480 $m\mu$. The molecular extinction coefficients of the maxima decreased from 89 to 61 with the increase of time of melting from one hour to 24 hours.

The paramagnetic susceptibility of the glasses initially decreased with increasing the melting time from half an hour to two hours and then

slightly increased to attain a constant value after eight hours after which no significant change was noticed.

The ratio of Mn^{3+} to the total manganese increased with prolonged time of melting and attained a stable value at about two hours.

Effect of oxidising or reducing substances: Changes in the redox conditions were obtained by introducing soda as sodium nitrate or by adding arsenious oxide and oxalic acid or starch to the glass batch (Fig 5).

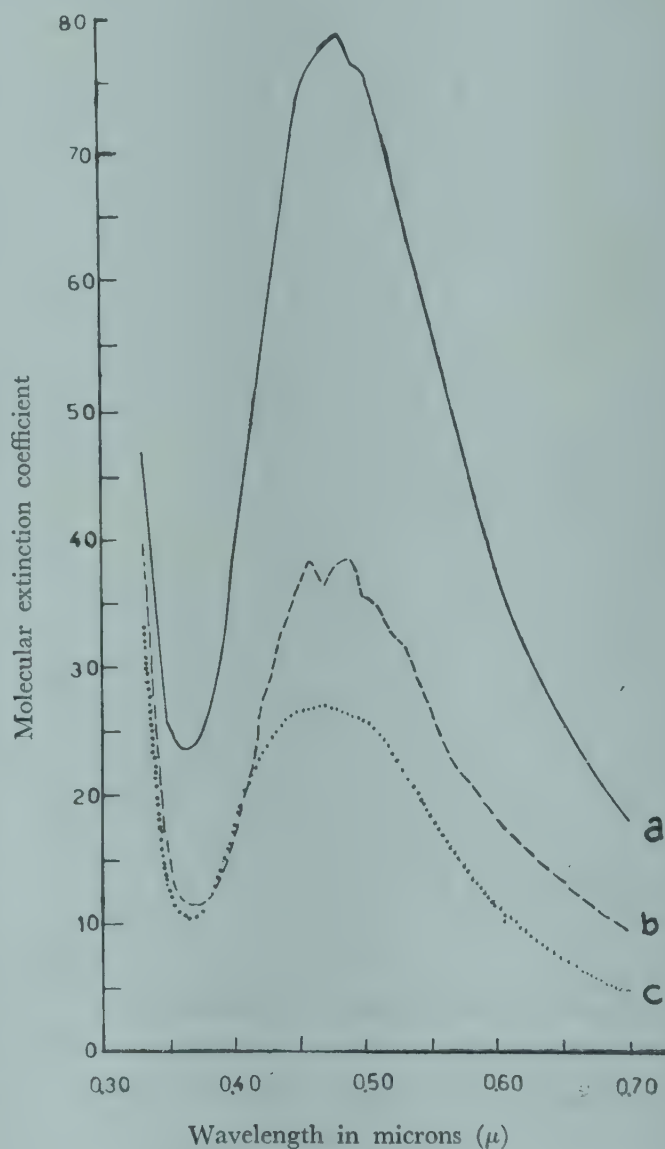


Fig 3
Effect of temperature of melting on the composition B_2O_3 70, Na_2O 30 wt per cent containing 0.20 gm MnO_2 per 100 gm glass: (a) melted at 900°; (b) melted at 1000°; and (c) melted at 1100°

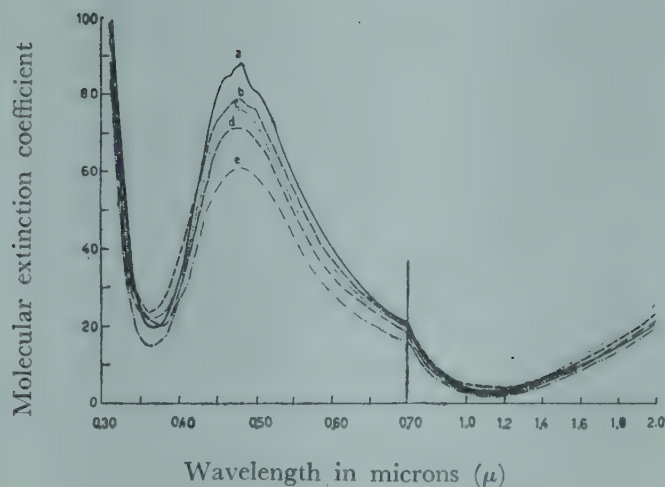


Fig 4

Effect of time of melting on the extinction curves of sodium borate glasses of the composition B_2O_3 70, Na_2O 30 wt per cent containing 0.20 gm MnO_2 per 100 gm glass: (a) glass 25; (b) glass 7; (c) glass 27; (d) glass 28; and (e) glass 30

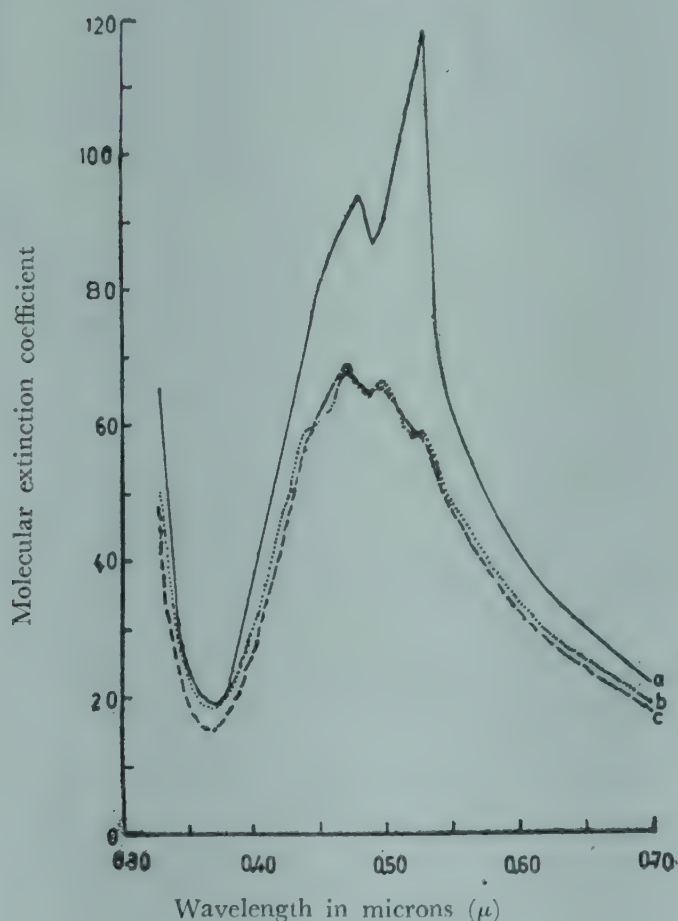


Fig 5

Effect of the oxidising or reducing substances on the extinction curves of sodium borate glass of the composition B_2O_3 70, Na_2O 30 wt per cent containing 0.20 gm MnO_2 per 100 gm glass: (a) soda was introduced as sodium nitrate; (b) 0.10 gm As_2O_3 + 1 gm oxalic acid; and (c) 1 gm starch was added

A glass containing starch showed the same absorption band as the normal glass with a slight decrease in the intensity of the band peak. A glass containing arsenious oxide and oxalic acid showed band of divalent manganese with no sign of trivalent manganese. The glass prepared by sodium nitrate showed two dominant peaks with maxima at about 480 and 530 $m\mu$.

Discussion

Condition of manganese ions in glasses: In glasses containing manganese, equilibrium is established between manganous and manganic ions depending on the composition of the base glass and the melting condition.

The main absorption of trivalent manganese ions comes from the ${}^5E_g \rightarrow {}^5T_{2g}$ in octahedral transition^{5-7,12-14}. It is the only spin-allowed transition expected in high spin d^4 system. A most important feature of its ground state is that according to the Jahn-Teller theorem, it must cause distortion in the surrounding octahedron and this distortion should be of appreciable magnitude because of the odd number of E_g electrons one in this case.

The effect of the concentration of manganese: A splitting was observed in glasses with low concentrations of manganese ions and is also observed with glasses containing high alkali oxide content. In the two cases, the proportion $Mn^{3+}/\Sigma Mn$ was relatively high. A splitting was observed in glasses containing 0.50 gm MnO_2 and was also noticed with glasses containing low alkali oxide content (10-20 wt per cent).

The reasoning for the first splitting of bands might be the presence of new coordination state of the Mn^{3+} ions as observed in the optical absorption of other transition metal ions^{1,5-7}.

A possibility for the second splitting is that distortion of the spinel structure of the Mn_3O_4 in which the Mn^{2+} ions are tetrahedrally coordinated and Mn^{3+} ions is in octahedral coordination. Each of the latter sites tends to distort its own octahedron and the cumulative

effect is that the entire lattice is distorted from cubic to elongated tetragonal¹⁵. G. Davies and K. Kustin¹⁶, T. S. Davies *et al*¹⁷ attributed splitting of the Mn^{3+} ions in solution of complexes to the tetragonal distortion. W. Levason and C. A. McAuliffe¹⁸ have shown that the electronic spectra of Mn^{3+} compounds are of special interest because the ground state anticipated in the octahedral complex 5E_g , is subject to strong Jahn-Teller forces^{7,10,13,15,19,20}.

In the case of manganese which exists in two valence states in the glasses, electron transfer or partial covalence can take place at favoured orbital overlaps. This tendency increases with the increase in the concentration of the manganese.

A similar conclusion was arrived at by Bh. V. Janakirama Rao²¹. An interesting assumption due to D. Reinen²² is that the distortion of the octahedral groups of Cu^{2+} ions at very low concentration is dynamic, *ie*, the long preferred axis of the octahedron changes between the three possible directions, so that in a time average an undistorted octahedron results. When a certain limiting concentration of ions is reached, cooperative elastic interactions between the individual CuO_6 polyhedra in the lattice lead to a fixation and energetically favourable orientation of the long axes of the octahedra units in relation to one another (static Jahn-Teller effect) and hence to a macroscopic symmetry effect of the host lattice structure.

The enhanced intensity of the absorption bands indicates larger distortion of the already distorted Mn^{3+} ions. This extra distortion produces more asymmetry and shifts it further away from the centro-symmetric group and this produces a higher intensity in the d-d band.

The effect of the condition of melting: The change in the condition of melting either by altering the duration of melting or increasing the melting temperature was found to change appreciably the absorption spectra and magnetic susceptibility of the glasses.

According to several authors^{1,23}, the increase in the temperature of glass generally favours

those compounds in which the metal has a lower valency.

In the glasses studied, both the trivalent and divalent manganese ions existed together.

Shorter time of melting (up to 4 hours) did not give the glass the proper time for the colour centre to reach an equilibrium state.

Increasing the time of melting (up to 48 hours) increased the proportion of the divalent manganese.

The relatively high fluidity of the alkali borate glasses studied allowed the equilibrium to reach in about 5 hours. The results of chemical analyses and magnetic measurements are in support of this assumption. A similar result was obtained by A. Paul and D. Lahiri¹⁰.

Magnetic susceptibility: The change in the environment influences the susceptibility of the multivalent paramagnetic ion through one or more of several means, such as^{21,23,24}: (i) shifting the oxidation-reduction equilibrium of the paramagnetic ion, (ii) creation of inhomogeneous electric fields around the paramagnetic ion to cause splitting of multiplet levels and consequent redistribution of the magnetic susceptibility, (iii) alteration of the coordination number of the paramagnetic ion, and (iv) alteration of the ionic character of the system.

Summary

Absorption spectra, magnetic susceptibility and chemical analysis of sodium borate glasses containing manganese were studied. The effect of the concentration of manganese ions and the form in which it was added and the condition of melting on the Mn^{2+} — Mn^{3+} equilibrium in these glasses was studied.

The absorption band due to trivalent manganese showed splitting into two or three peaks. A number of probable reasons have been suggested.

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PERMITTIVITY IN THE MICROWAVE REGION OF SOME SILICATE AND FERRITE MINERALS AT LOW PRESSURES

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Introduction

The permittivity and dielectric loss in the microwave region can be determined by several methods¹⁻⁶. In the present work, a method⁵ which depends on standing wave measurements in a rectangular waveguide is used.

Let the waves propagating from the source be incident normally at the surface of the material of dielectric constant ϵ^* . The reflection coefficient R is given by, $R = |R|e^{i\phi}$, where ϕ is the phase change on reflection. As a result of reflection, a standing wave pattern is produced and from the shape and position of this pattern ϕ and $|R|$ can be obtained.

From the transmission line theory, $R = (1-S)/(1+S) \cdot e^{i\phi}$, where S is the reciprocal of the standing wave ratio. If S_0 and S_s are the reciprocal of the standing wave ratio in the open and short circuited cases, the reflection coefficient $|R|$ for the two previous cases denoted by $|R_0|$ and $|R_s|$ can be calculated.

According to J. H. Heath and E. T. Clothier⁷, the attenuation (α) in decibels for very low loss materials can be calculated from:

$$\alpha = 10 \log \frac{|R_0| + |R_s|}{2} \quad \dots (1)$$

From the standing wave ratio and phase shift, the input impedances r_0 and r_s in the open and short circuited cases can be calculated using the Smith Chart and used to find ϵ' and ϵ'' from⁸ equation 2:

$$\frac{1}{r_0 r_s} = \frac{\epsilon' - q}{1 - q} - i \frac{\epsilon''}{1 - q} \quad \dots (2)$$

where, $q = \lambda/\lambda_c$, λ is the wavelength in air and λ_c is the cut off wavelength. ϵ' and ϵ'' can be obtained by equating the real and imaginary parts of equation 2. The values obtained are the measured values and can be denoted by ϵ'_m and ϵ''_m and can be used to calculate ϵ' and ϵ'' of the material from⁹⁻¹¹ equations 3 and 4:

$$\epsilon'_m = 1 + P (\epsilon' - 1) \quad \dots (3)$$

$$\text{and } \epsilon'' = \frac{\epsilon''_m}{P} \quad \dots (4)$$

where, P is the density of packing of the materials as given by the ratio of the volume of the material to the overall volume occupied. The volume of the material is obtained from the mass divided by density and the overall volume occupied from the dimensions of the space occupied by the material. The accuracy in ϵ' is better than 5 per cent.

Experimental

The apparatus used for the measurements of permittivity and attenuation caused by the inserted samples in the microwave region is described elsewhere⁸. The cell used in all the measurements was a piece of waveguide (4 cm long) closed from both sides by thin mica windows. The cell was closed by a shorting metal plate for the measurements in the short circuited case. For the measurements in the open circuited case, the cell was connected to a movable short adjusted to interpose a $\lambda/4$ air-filled waveguide between it and the back face of the test material.

Measurements were carried out on clinostatite, forsterite, magnesioferrite, magnesio-

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chromite, β -dicalcium silicate and tricalcium silicate. Each sample was dried at 200° for six hours till a constant weight was attained before use and compressed inside the cell by means of a plunger and an oil press. The voltage standing wave ratio was determined¹² by taking the probe positions Δx at which the power equalled twice its minimum value and substituting in equation 5:

$$S = 1/\sigma = \pi \Delta x / \lambda_g \quad \dots (5)$$

Also, from the position of the first minimum from the interface, ϕ could be computed. Knowing S_0 , S_s and ϕ the values of r_0 and r_s could be obtained and used to find ϵ' and ϵ'' .

Materials

Clinoenstatite and forsterite: Clinoenstatite and forsterite minerals have good dielectric properties and are used in the production of insulators for high frequency equipment.

Clinoenstatite ($\text{MgO} \cdot \text{SiO}_2$) minerals were prepared synthetically from finely ground mixtures of magnesia and silica in the molecular proportion of 1:1 and 2:1 respectively. The homogeneous mixtures were fired for two periods of 10 hours at 1350° in case of clinoenstatite and 1600° in case of forsterite with intermediate grinding.

Magnesioferrite and Magnesiochromite spinel: Magnesioferrite ($\text{MgO} \cdot \text{Fe}_2\text{O}_3$) and magnesiochromite ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$) spinels are important in high frequency engineering. They play a dual role as materials with high electric resistance and as nonmetallic.

Magnesioferrite spinel was obtained synthetically from the finely ground mixture of MgO and Fe_2O_3 in a stoichiometric ratio. Homogenisation of the mixture in a special steel ball-mill was carried out for 6 hours followed by firing to the sintering point at temperatures ranging between 1000 and 1300° in the presence of a stream of oxygen.

Magnesiochromite was prepared synthetically from a mixture of finely ground MgO and Cr_2O_3 in the molar ratio 1 : 1. The presence of 0.5 to

1 per cent excess Cr_2O_3 was necessary due to sublimation of Cr_2O_3 . The homogeneous mixture was fired at 1200° for 6 hours followed by grinding and firing at 1200° for another 6 hours. The product was reground, moulded and finally fired at 1600° for 10 hours. Chemical analysis was necessary to ascertain that MgO and Cr_2O_3 molar ratio was always 1 : 1.

β -dicalcium silicate and tricalcium silicate: β -dicalcium silicate ($2 \text{ CaO} \cdot \text{SiO}_2$) and tricalcium silicate ($3 \text{ CaO} \cdot \text{SiO}_2$) minerals are present in Portland cement. β -dicalcium silicate mineral inverts on cooling at 675° to the γ -dicalcium silicate.

Standard β -dicalcium silicate was obtained by heating a mixture of finely ground CaO and SiO_2 in the molecular ratio 2 : 1 at 1450° . The process of regrinding and reheating was repeated until the mixture was homogeneous. The product was then reground, moulded and finally fired at 1600° for 10 hours. The product was then cooled slowly till 1000° and then quenched in air to obtain the β -dicalcium silicate.

Tricalcium silicate is stable only over a limited temperature ranging from 1250 - 1900° and decomposes both above and below this range into dicalcium silicate and CaO .

Tricalcium silicate was obtained by heating a mixture of CaO and SiO_2 in the molecular ratio of 3 : 1 at 1200° for 6 hours. The process was repeated until the combination was complete. The product was then ground, moulded and fired at 1600° for 10 hours followed by quenching rapidly in air. X-ray diffraction patterns of the prepared minerals proved their complete formation.

Results and discussion

The minerals were pressed in the cell under low pressures less than 100 kg/cm^2 . The packing density P was calculated from the specific gravity of the samples and the dimensions of the cell. The true value of the dielectric constant ϵ' was calculated from the measured value ϵ'_m using equation 3. Also, the attenuation

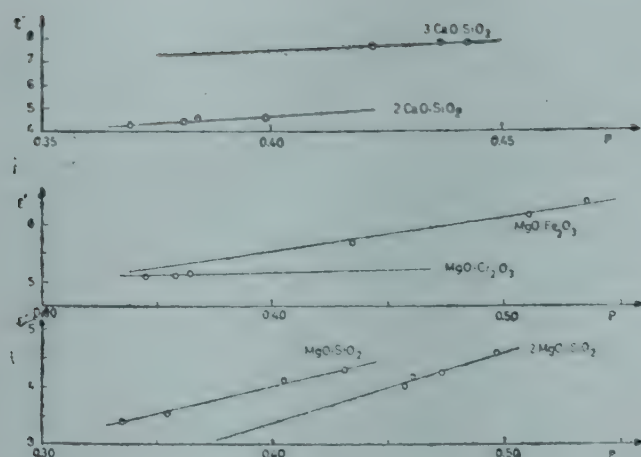


Fig 1
Dielectric constant ϵ' vs packing density P for the different samples

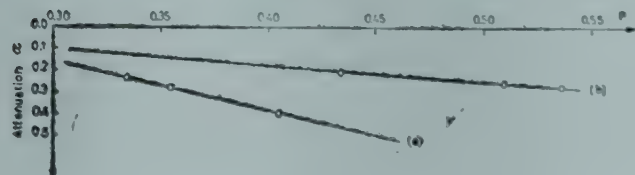


Fig 2
Attenuation α vs packing density P for: (a) MgO.SiO_2 and (b) $\text{MgO.Fe}_2\text{O}_3$

(α) was calculated using equation 1. The results obtained for ϵ'_m , ϵ' and α are given in Table I.

Table I shows the calculated volumes of the crystals using the estimated radii and the ratios of the atomic weight to the corresponding volume. This ratio was proportional to the packing density in the crystal (Table I).

The relation between ϵ' and P is illustrated in Fig 1. ϵ' increased linearly with P , i.e., with the increase in pressure. Similar behaviour was found in the case of titanate ceramics¹³. For each group, the mineral of lower specific gravity had the higher dielectric constant at the same packing density. ϵ' for calcium compounds, at any pressure, was higher than the magnesium compounds. This was noticed also in the case of Mg and Ca-titanates¹³.

Attenuation of the samples in decibels at different packing densities is shown in Fig 2. The curves show that MgO.SiO_2 having the smallest radius of all the investigated magnesium minerals exhibited the highest attenuation, while

TABLE I

Dielectric constant ϵ' and attenuation α

Material	r (Å)	V (Å) ³	Atomic weight	At wt V	Specific gravity	P	ϵ'_m	ϵ'	α (db)
Clinoenstatite (MgO.SiO_2)	5.28	630	100	0.160	3.19	0.335	1.80	3.39	-0.235
						0.355	1.89	3.51	-0.280
						0.405	2.27	4.13	-0.400
						0.432	2.41	4.27	
Forsterite (2MgO.SiO_2)	7.34	1630	140	0.012	3.22	0.458	2.37	3.99	-0.240
						0.461	2.46	4.17	-0.255
						0.474	2.52	4.21	-0.275
						0.497	2.68	4.37	
Magnesiochromite ($\text{MgO.Cr}_2\text{O}_3$)	7.52	1740	192	0.011	4.39	0.345	2.41	5.09	-0.192
						0.358	2.47	5.11	-0.203
						0.363	2.51	5.16	
Magnesioferrite ($\text{MgO.Fe}_2\text{O}_3$)	7.54	1805	200	0.011	4.20	0.435	3.03	5.67	-0.205
						0.511	3.63	6.16	-0.255
						0.536	3.90	6.40	-0.280
β -dicalcium silicate (2CaO.SiO_2)	8.00	2150	168	0.078	3.28	0.369	2.19	4.22	-0.150
						0.381	2.29	4.39	-0.270
						0.384	2.37	4.57	-0.300
						0.399	2.40	4.52	-0.400
Tricalcium silicate (3CaO.SiO_2)	10.39	4720	228	0.040	3.15	0.422	3.78	7.60	-0.255
						0.437	3.95	7.74	-0.275
						0.443	3.97	7.73	-0.300

MgO.Fe₂O₃ having the largest radius showed the lower attenuation. The attenuation of the other samples was in between these two curves. This may lead to the conclusion that the attenuation in this frequency range depends upon the dimensions of the crystal. Since MgFe₂O₄ has low attenuation and high electrical resistance (known to be between 10² and 10⁸ ohm cm), it could be used as cores in high frequency coils, and tricalcium silicate which possessed high dielectric constant and low attenuation (Table I) could be used as an insulator.

The dielectric loss ϵ'' of the investigated materials was low and the reflection method

adopted here was not suitable for its determination. A method described by S. Roberts and A. Von Hippel⁵ using two sample lengths is more convenient but is difficult to press two samples under the same pressure and so could not be measured by the method used in this work.

Summary

Dielectric permittivity and attenuation of clinoenstatite (MgO. SiO₂), forsterite, magnesioferrite (MgO. Fe₂O₃), magnesiochromite (MgO. Cr₂O₃), β -dicalcium silicate and tricalcium silicate were studied at low pressures.

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IMPROVING THE PERFORMANCE OF GLASS MELTING TANK FURNACES

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Introduction

For getting efficient performance of a glass melting tank furnace a good design is most important. Designs for such furnaces are usually imported from world's three or four best furnace designers of glass melting tank furnaces. It may so happen that different firms in India may import the same design from any one of these firms, leading to unnecessary drainage of foreign exchange. Such foreign designers have decades of experience in this line and case studies behind them which we do not have. A beginning has to be made to develop indigenous design capability for such furnaces. Central Glass and Ceramic Research Institute is in a position to help in this task and to collaborate with indigenous designers having requisite expertise and skilled personnel in such development.

Oil fired glass tank furnaces

For oil fired container glass tanks up to 100 tonnes per day, end regenerative underport fired furnaces have come to be recognised as most suitable. Working end has been much reduced in size and entirely separated from melting zone with its own independent firing. The main reason for such a development was the need for independent control of temperature of working end. The early collapse of the silica shadow wall was also a reason thereof. However, that difficulty could be overcome by use of fusion cast or some other superior material for the shadow wall.

Gas fired furnaces

When gases of high calorific value like natural gas or coal gas are used for firing, the same arrangement of end regenerators will be the most suitable. When firing is by producer gas, locating the regenerators at the ends is not the usual custom from spatial and design considerations. The regenerators will be at the sides of the tank and that is the main reason for the inefficiency of producer gas *vis-a-vis* furnace oil.

Design features

The most important parts of a furnace on which the overall performance depends are: the ports and regenerators, other parts being more or less standardised in dimensions and shape.

Ports: For oil fired furnaces, broad and shallow ports give the best result. Such ports, with optimum angles of port sill and arch and with the use of suitable burners forming an integral part of the combination, which render the flames sweeping along the glass surface without bouncing off it, give the best result.

In producer gas fired furnaces of the usual type with built in brick producers, there are too many ports. By reducing the number of ports, surface heat loss is reduced as well as more space for the buckstays and operational requirements is obtained. Here the port design should be such as to give a flame gently sweeping along the glass surface. Some degree of turbulence for mixing air with gas is necessary but too much of it is to be avoided.

Regenerators: The regenerators are to be such

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as to give maximum recovery of waste heat, in other words, heating the required amount of gases to the highest temperature possible. To achieve this the heat transfer coefficient from the waste gases to the air or producer gas and the surface of checker bricks should be as large as possible. The heat transfer coefficient depends on the size of the checker openings and on the velocity of the gases. There is a lower limit to the size of the checker openings arising from the danger of their clogging up. For a campaign of about 2 years the minimum size appears to be 6"×6". For longer campaigns 7.5"×7.5" or even 9"×9" would be advisable. The velocity of the waste gases entering the checkers should not exceed above 6 ft/sec from considerations of pressure loss. So, the only way of increasing the efficiency of the regenerator is by increasing the surface of checker bricks or in other words the size of the regenerator. The important point to note is that the size is to be increased vertically and not horizontally. In a factory recently visited by the author, they had provided inordinately large (horizontally) regenerators in an attempt to increase the surface of checkers, the height of checkers being only about 6 ft or so. Such big regenerators while increasing the surface heat losses did not give any corresponding gain in heat recovery as the heating surface was increased at the expense of velocity.

Tall regenerators not only give increased heat recovery, but they also increase the available draft to pull the secondary air. While checker heights of 12-15 ft are usual in some of the good oil fired furnaces, some furnaces of imported design have heights even above 25 ft. In such cases it is better to have rider arches also in the middle of the checkers to provide stability. If due to any reasons it is not possible to have such tall chambers, double pass regenerators are used to get the total length of travel of gases of 20-25 ft. Double pass regenerators have advantage of ease of setting of checkers, ease of their cleaning and possibility of using different arrangements of bricks in the two chambers. The smaller outer chamber gives a greater velocity

to the gases than what is possible in a single regenerator. However, aerodynamically this arrangement is not very good as lateral distribution of gases in the outer chamber may not be uniform and there may be some dead corners. The surface heat losses will be somewhat more than in single chamber of corresponding size. Also secondary air cannot be sent in satisfactorily without use of an air blower.

Distribution of available plan area of regenerator into optimum length and breadth is also very important. Length is related to the velocity of the waste gases, the consideration being the avoidance of dead pockets at the ends of the regenerators. In long regenerators giving a downward turn to the regenerator arch is helpful. Breadth is related to the breadth of the port, the consideration being uniform lateral distribution of gases. In broad regenerators, inclining the port horizontally at an angle of 5-10° or so helps in keeping the flames away from the side walls.

In producer gas fired tanks height of checkers in air regenerators can be as much as 20 ft or more. Height of checkers in gas regenerators should be about half of that, as gas should not be heated to more than about 900° or so for well known reasons. Ratio of plan area of air and gas regenerators normally varies from 1.5-2.0 depending on composition and temperature of producer gas.

Insulation

After suitable design, prevention of surface losses by suitable insulation is very important. The beneficiation arising from insulation can be gauged from the fact that the overall exposed area of the whole furnace is about 10 times the melting area in end regenerator furnaces and about 13 times in side regenerator furnaces. The necessity for insulation has been recognised by glass factories; only the difficulty arising therefrom stand in the way of its proper implementation.

Insulation of crown: Crown is the portion from where maximum loss of heat takes place. Crown

of working end is usually insulated. But opinion varies regarding insulation of crown of melting zone of soda lime container glass tanks. In some cases insulation has affected the life of the crown. Such an occurrence cannot be due to temperature alone, as the refractoriness under load of silica bricks is over 1630° whereas the melting zone temperature is below 1500° usually. If the failure is due to impingement of flames on the crown the remedy is obvious. The cause of the deterioration can only be due to attack by alkali vapour. Hence, the quality of the silica bricks used is to be considered. The alkali vapour can attack the inner surface; it can also see through the joints and condense therein attacking the brick, gradually forming fusible silicates of relatively high viscosity which can drop in the glass, forming defects. The vapours in due course can go to the outer surface and attack there also.

Attack to the inner portion of the brick depends on the porosity of the bricks, the furnace temperature and pressure. Use of bricks of a little lower porosity, if available, would be preferable. Reduction of furnace pressure, if possible, will also help. It is claimed that impregnating the silica bricks up to a depth of 2-4 inches with a solution of orthophosphoric acid in water will improve their corrosion resistance.

To minimise corrosion of joints, use of bricks true in size and shape, *ie*, without warpage is necessary. This is, however, not so easy in practice as the general complaint against indigenous refractories is on these points of shape and size among others. Use of bricks ground flat would solve this. Laying the crown dry, *ie*, without mortar will not be advisable as thereby, the alkali vapours can easily enter the joints exposed due to the warpage and attack them. Use of suitable cement, low in Al_2O_3 for laying the bricks properly are considered essential. After construction, a thorough grouting with a thin silica cement slip will help in filling all joints.

Silica based insulating bricks are used to insulate silica crowns. Use of a thin layer of silica sand below the insulating brick will be further

protection against attack by alkali vapours. During heating of the furnace the tension of the tie rods is to be such that the inner joints are not open, which will happen if the tie rods are not tightened when the silica crown sags down a little after it has attained full temperature during heating of the tank. The expansion joints are also to be filled up (after the tank heated up) with a stiff silica cement, to prevent out flow of alkali vapours.

Insulation of super structure: It is of next importance in saving surface heat loss. Fused cast material for the inner lining enables insulation up to even a thickness of 9 inches. But this is not possible for all due to the cost or non-availability of fused cast material. So, silica or sillimanite are usually used for the superstructure and an insulation of 3-4.5 inches only is used. Some have discontinued insulation as the inner lining was getting affected. Here also the alkali dust or vapour are the corroding agents and selection of inner refractory of suitable quality and laying cement together with proper technique will remedy this. Insulation may be done only over inner lining of 12-13.5 inches. There is no risk at all in insulating the superstructure of the working end. Burner blocks and stuckstones of fused cast material may also be insulated with ceramic felt of about 1 inch thickness to save heat loss.

Insulation of tank basin: Below glass level in melting zone, when side walls are made of fusion cast material insulation as per established procedure is the usual practice in developed countries. Experience in India has not been happy. Some have done such insulation without any trouble while others had to remove such insulation due to deterioration of the inner material. The reasons for such deterioration should be analysed. If it is due to not leaving the joints open, the same should be done. If insulation was done directly against the fused cast material use of a 3 inch fireclay tile between the insulation and fused cast material will be helpful.

Insulation of bottom: Insulation of the bottom of the tank is the established practice abroad. It

is possible only with the use of suitable fused cast or zircon or zirmul paving. A few factories in India have also insulated the bottoms with good benefit. They have used locally made zircon brick paving. Zirmul paving is thought to be even better. But cost of such material is very high even at par with imported fused cast material. If prices could be reduced, more and more factories could use them. Cost of such paving can be made good by the fuel saved.

Insulation of ports: For ports, either sillimanite or silica (for sides and crown) are used. Many have insulated them up to 3-4-5 inches with success. Use of magnesite material by some factories has enabled a thicker insulation and also a longer campaign. There is no risk involved and much to be gained by insulating thoroughly the entire regenerator region after using suitable inner material. Many factories are doing this with good results.

High cost of material is again the reason for not using basic material for checkers and walls, etc, of regenerators though their advantages in giving improved performance and long trouble-free life are well known.

To sum up this aspect of insulation, it can be done only if suitable material is used for inner lining and when it is laid with suitable cement. Quality of refractories available indigenously has been questioned by the glass industry. When quality is suitable cost is high. Refractory manufacturers should take up this challenge and supply suitable refractories at a reasonable cost. It will not be incorrect to state that the improvement of furnaces is closely linked with the development and supply of suitable refractories.

Operation

The third important factor on which the performance depends is operation which comprises equipment used for firing, instrumentation used for control of combustion conditions and operational technique.

Firing equipment: Very good performance of furnaces of imported design is partly due to the imported firing equipment used. As good firing

equipment are not made indigenously, manufacture of these items should be taken up early; till that time, allowing the import of such equipment will be a pragmatic policy in the interest of fuel economy.

Instrumentation: Combustion control equipment is equally important as firing equipment. They are installed whenever available indigenously. General complaint has been about their quality and maintenance. Instruments not available indigenously should be allowed to be imported in order to save fuel.

Operational technique

Controlling excess air by automatic instrumentation using orsat apparatus should be adopted. Furnace pressure should be kept low as far as possible.

The burner angle is to be adjusted to the optimum after trials. The angle may vary between 5° and 8° depending on type of burner and port geometry. Some factories are using burners in a horizontal position or even inclined downwards (in underport firing) with the idea that flames will then graze along the glass surface. Burners tilted up at above stated angle and located as near as possible from glass surface and port sill seem to be the best arrangement.

Injecting oxygen from below the burner block in oil fired furnaces has been found to improve performance. In natural gas fired furnace, mixing oxygen with secondary air is observed to give better performance. Same could be tried in our producer gas fired furnaces.

It is claimed that by treating fuel oil with a nitrogenous manganese complex, the flue gas losses can be reduced. Details are not available.

An indigenously available addvite to furnace oil is claimed to dissolve and utilise for burning the oil sludge, thereby saving 3 per cent of fuel oil. It is also claimed to reduce corrosion of chimney by sulphur trioxide in flue gases.

The glass level is to be kept as high as possible to increase heat transfer.

The possibility of reducing the air cooling of

TABLE I

Comparative requirement and cost of energy from different fuels for melting one tonne of glass

Fuel	Requirement of fuel per tonne of glass in 40-50 tonnes/day container glass tanks		Cost of fuel at which each will be at par with furnace oil at Rs 1,000/tonne	
	Quantity	Heat content		
Furnace oil	0.2 tonne	80 therms	Rs 1000/tonne	2.50/Th
Coal	0.6 tonne	120 „	Rs 333/tonne	1.66/Th
Natural gas	10,000 cft	90 „	Rs 20/1000 cft	2.25/Th
Coal gas	18,000 cft	90 „	Rs 11/25/cft	2.25/Th
LP gas	0.173 tonne	80 „	Rs 1150/tonne	2.50/Th
Electricity	900 kWh	30 „	22.5 paise/unit	6.40/Th

the fusion cast basin blocks has to be studied. When sillimanite blocks are used, this is possible and should be the practice.

The possibility of improving the air pre-heat by some unconventional methods (when it is not possible by usual methods) is to be studied. Such methods are mixing of soot or some moisture with the air to improve its heat acceptance by radiation and also mixing a small part of waste gases with the air for the same reason.

A better glass to fuel ratio is possible by making the glass batch more easy to melt and fine. Apart from the use of fluxes, use of blast furnace slag is found to give this benefit. Replacing a small part (up to 0.5 per cent) of Na_2O by Li_2O is also claimed to give similar advantage. In Japan very great improvement of melting rate is claimed by using caustic soda in place of soda ash in the batch. This may have to be tried here in small steps only. Wherever available use of fine grained sand such as ($-50+100$) may be tried.

Economics of firing, *ie*, cost of fuel consumed is also a factor to be considered. Table I indicates the comparative costs of different fuels for melting one tonne of glass.

With the finding of more oil wells by Oil and Natural Gas Commission, availability of natural gas is likely to improve. It can be used in place of oil to minimise the fuel cost.

Summary

Importance of a good design for efficient performance of a glass melting tank furnace has been emphasised. Characteristic design features for ports and regenerators for oil fired and producer gas furnaces are also discussed.

Insulation of all portions of the furnace is possible if suitable inner refractory material is used. Details of insulation of different parts are indicated.

Use of firing equipment, suitable instrumentation for control of combustion conditions, burner angle and level of glass are discussed.

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Development of acid resistant base frits for coloured enamels. M. C. Ghose and S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (2) 31-35 (1977).

Effects of the variation of titania and zirconia in the base enamel frits on their fusion flow characteristics and on the acid resistance and colour stability of the fired coatings using cadmium-selenium colours were studied.

Effect of mineralisers on the mullite formation in kaolin clays. P. S. Aggarwal, M. K. Banerjee and R. V. Lele, *Cent Glass Ceram Res Inst Bull*, **24** (2) 36-39 (1977).

The effect of mineralisers on the mullite formation in kaolins was studied. Ordered and disordered kaolinites of four types were used. It was observed that the mineralisers did not increase the amount of mullite in kaolinites heated at 1400°.

Improvement in brightness of off-coloured ceramic raw materials by chemical decolourisation process. S. R. Das and S. K. Guha, *Cent Glass Ceram Res Inst Bull*, **24** (2) 40-42 (1977).

Improvement in brightness made by the chemical decolourisation process of ceramic raw materials including clay, pyrophyllite, bauxite, silica-sand, received from different regions of India were studied. Overall brightness and reduction in percentage Fe_2O_3 in most of

the minerals could be achieved by this process.

Thermoluminescence response of quartz and some silicate glasses to gamma rays and uv radiations. M. M. Morsi and M. A. Gomaa, *Cent Glass Ceram Res Inst Bull*, **24** (2) 43-48 (1977).

Thermoluminescence (TL) of natural quartz, soda-silica and soda-lime silica glasses with and without Cu^+ ions to γ -rays and uv radiations were investigated. Natural quartz was found to have good TL response to the low γ -ray doses. The increase of Na_2O content decreased the TL response of soda-silicate glasses to γ -rays. Doping of soda-lime glasses with Cu^+ ions increased greatly its TL response to both low and high doses of γ -rays and uv radiations.

Microindentation hardness of glasses: Part I—Cabal glasses. H. A. El-Batal and N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **24** (2) 48-59 (1977).

Indentation tests were made with the Vickers diamond pyramid on various cabal glasses having the base composition of CaO 30, B_2O_3 40 and Al_2O_3 30 wt per cent with the replacement of parts or all the lime by alkali or alkaline earth oxides or of boric oxide by silica, titania or zirconia. The effect of the load of indentation was investigated and the results obtained were correlated with the Littleton softening points.

CENTRAL GLASS AND CERAMIC RESEARCH INSTITUTE BULLETIN

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Mise au point d'une masse frittée résistante aux acides pour les émaux colorés. M. C. Ghose et S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (2) 31-35 (1977).

On examine les effets des variations de la teneur en titane et en zircone de masses frittées sur leurs caractéristiques de la coulée, et sur la résistance aux acides et de la stabilité de teintes à la cuisson en utilisant des colorants obtenus à partir de cadmium-sélénium.

Influence de minéralisateurs sur la formation de mullite dans les argiles kaoliniques. P. S. Aggarwal, M. K. Banerjee et R. V. Lele, *Cent Glass Ceram Res Inst Bull*, **24** (2) 36-39 (1977).

On étudie dans cet article l'influence des minéralisateurs

sur la formation de mullite dans les kaolins. On utilise quatre types de kaolinites ayant des structures à la fois en ordre et en désordre. On constate que les minéralisateurs ne permettent pas d'augmenter la teneur en mullite dans les kaolinites chauffées à 1400°.

Amélioration du brillant et des couleurs des matières premières au moyen de décoloration chimique. S. R. Das et S. K. Guha, *Cent Glass Ceram Res Inst Bull*, **24** (2) 40-42 (1977).

L'amélioration du brillant des matières premières céramiques, à savoir, l'argile, la pyrophyllite, la bauxite, le sable siliceux etc. provenant de différentes régions de l'Inde est réalisée au moyen de décoloration chimique. Cette méthode permet d'abaisser la teneur en Fe_2O_3 de la plupart des minéraux.

Réponse thermoluminescence du quartz et des verres silicatés exposés aux rayons gamma et aux radiations uv. M. M. Morsi et M. A. Gomaa, *Cent Glass Ceram Res Inst Bull*, **24**(2) 43-48 (1977).

On examine la thermoluminescence du quartz naturel, des verres sodosilicatés et des verres silicosodocalciques avec des ions Cu^+ et sans ions Cu^+ exposés aux rayons γ et aux radiations uv. On accuse une bonne réponse thermoluminescence dans le quartz naturel exposé à une faible dose de rayons γ . L'augmentation de la teneur en Na_2O abaisse la réponse thermoluminescence des verres sodosilicatés exposés aux rayons γ . Lorsqu'on dope les verres sodocalciques par des ions Cu^+ , on constate une augmentation considérable de leur réponse thermoluminescence à la

fois à faible et à forte doses de rayons γ et aux radiations uv.

Microdureté des verres. Première Partie. Verres Cabals. H. A. El-Batal et N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **24** (2) 48-59 (1977).

Des essais d'empreintes de dureté ont été effectués à l'aide d'une pyramide de Vickers sur différents verres cabals ayant la composition de base CaO 30 B_2O_3 40 et Al_2O_3 30 (en % pondéral) par le remplacement partiel ou total de la chaux avec l'alcali ou avec les oxydes alcalinoterreux ou par le remplacement de l'oxyde borique avec la silice, le titane ou la zircone. On étudie l'effet de la charge d'indentation et on met en corrélation le résultat obtenu avec le point de Littleton.

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Entwicklung von säurebeständigen Grundfritten für Farbemail. M. C. Ghose und S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (2) 31-35 (1977).

Einflüsse der Variationen von Titanoxid und Zirkonoxid in der Grundemailfritte auf Schmelzflusseigenschaften, und auf Säurebeständigkeit und Farbbeständigkeit vom gebrannten Belag mit Gebrauch von Kadmium-Selenium Farben wurden untersucht.

Einfluss der Mineralisatoren auf die Mullitbildung in Kaolin-Tönen. P. S. Aggarwal, M. K. Banerjee und R. V. Lele, *Cent Glass Ceram Res Inst Bull*, **24** (2) 36-39 (1977).

Der Einfluss der Mineralisatoren auf die Mullitbildung in Kaolin wurde untersucht. Vier sorten von geordneten und ungeordneten Kaolin-Tönen wurden benutzt. Es wurde beobachtet, dass es den Mineralisatoren nicht gelang, den Mullitgehalt in Kaolinit-Tönen, die bei 1400° geheizt wurden, erhöhen zu können.

Glanzverbesserung von fehlgefärbten keramischen Rohstoffen mit Hilfe des chemischen Verfärbungsverfahrens. S. R. Das und S. K. Guha, *Cent Glass Ceram Res Inst Bull*, **24** (2) 40-42 (1977).

Glanzverbesserungen, vollbracht mit Hilfe des chemischen Verfärbungsverfahrens, von keramischen Rohstoffen einschliesslich Ton, Pyrophyllit, Bauxit, Silikasand usw erhalten von verschiedenen Bezirken Indiens wurden untersucht. Gesamte Helligkeit und Verminderung von

Prozentgehalt Fe_2O_3 in meisten der Mineralien konnten durch dieses Verfahren erzielt werden.

Thermolumineszenz-Anregungen von Quarz und einigen Silikatgläsern von Gammastrahlen und UV Strahlungen. M. M. Morsi und M. A. Gomaa, *Cent Glass Ceram Res Inst Bull*, **24** (2) 43-48 (1977).

Thermolumineszenz (TL) von natürlichem Quarz, Natriumsilikat und Natrium-Kalziumsilikat-Gläser mit und ohne Cu^+ Ionen auf Gammastrahlen und UV-Strahlungen wurde untersucht. Es wurde gefunden, dass natürliches Quarz gute Anregungen auf die niedrigen Gammastrahlen gaben. Die Erhöhung von Na_2O -Gehalt verminderte die TL-Anregungen von Na_2O - SiO_2 Gläsern auf Gammastrahlen. Dotierung der Na_2O - CaO - SiO_2 Gläser mit Cu^+ Ionen erhöhte beträchtlich ihre TL-Anregungen auf die niedrigen, sowie die erhöhten Gaben von Gammastrahlen und UV-Strahlungen.

Mikro Eindringungshärte von Gläsern: Teil I - "Cabal" Gläser. H. A. El-Batal und N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **24** (2) 48-59 (1977).

Eindringungsverfahren mit Hilfe der Vickers Diamantpyramide auf verschiedene "Cabal" Gläser wurde durchgeführt. Diese "Cabal" Gläser hatten die Grundzusammensetzung von CaO 30, B_2O_3 40 und Al_2O_3 30 Gewichtsprozent mit der Ersetzung eines Teils oder des Ganzen von CaO durch Alkali- oder Erdalkalioxide, oder B_2O_3 durch SiO_2 , TiO_2 oder ZrO_2 . Der Einfluss der Eindringlast wurde untersucht und die erhaltenen Ergebnisse wurden mit Littleton's Erweichungspunkte vergleicht.

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DEVELOPMENT OF ACID RESISTANT BASE FRITS FOR COLOURED ENAMELS

M. C. GHOSE AND S. S. VERMA*

Introduction

The mechanism of acid attack on the fired enamel coating is of a complex nature due to the heterogeneity of enamels which mainly comprise a glassy matrix¹. Highly acid resistant enamels are characterised by their high silica contents, low fluorine and boron contents and adjustment of the remaining constituents in such a way as to yield the other desired working properties of the enamel, *eg*, thermal expansion, fusibility, *etc*. Due to the above compositional limitations the acid resistant enamels, in general, possess higher refractoriness and viscosity. However, this is not conducive to obtain a satisfactory and uniform coloured enamel finish, particularly in the case of temperature sensitive cadmium colours and other delicate shades. The usual low acid resistance of coloured enamels may be attributed to the higher proportions of fluxes normally used in the base frit compositions for obtaining low melting compositions.

The objective of the present study was to develop highly acid resistant transparent base enamel frits without sacrificing fusibility and other working properties useful for obtaining satisfactory surface finish.

The oxides normally used in frit making have been arranged² in the following approximate increasing order in respect of the acid resistance they impart to the finished coating:



In order to increase the acid, alkali and water resistance as well as mobility of the enamels, the

influence of TiO_2 and ZrO_2 on transparent enamels was studied. A part of the results in respect of acid resistance and fusibility is presented in this paper. As the stability of Cd-Se red colour is substantially influenced by the nature of chemical constituents of the enamel composition, this aspect was also included under the present investigation.

Experimental

Two different batch compositions A and B corresponding to the same melted oxide composition of transparent base enamel were used to start with (Table I).

In the enamel composition A, CaO was added as calcium carbonate adjusting fluorine with sodium silicofluoride and in the composition B, CaO was obtained from fluorspar adjusting remaining fluorine by using sodium silicofluoride. In both of the batch compositions TiO_2 and ZrO_2 were separately increased in steps of 1.5 parts and continued up to total contents of TiO_2 at 11.50 parts and ZrO_2 at 9.00 parts. Cheaply available indigenous rutile ore and zircon were used as sources of TiO_2 and ZrO_2 . Batches of one to two kg were melted at 1200° in an oil fired crucible furnace under oxidising conditions. Mill additions used were clay (5 per cent), sodium nitrite (0.25 per cent) and water (45 per cent) with the base enamel frits both with and without the colouring oxides (Cd-Se red stain 2 to 4 per cent). The milling fineness was just —200 mesh standard BS sieve. The enamels under study were applied over white cover coated test pieces by dipping and fired at 800–820°. The application weight of the enamels was

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in the range of 2.5 to 3.0 gm/dm² surface area. Acid resistance studies of the fired coatings were carried out in accordance with IS: 3972-1968, 6.1, for citric acid spot test and ASTM: C-283-1967 for boiling acid resistance test. Fusion flow characteristics of the enamel frits was determined by measuring the length of the melted button as per ASTM: C-374-60 (method B). The stability of the Cd-Se red colour of the fired coating was studied by visual observation of the shade, density and intensity of the colour.

Results and discussion

The weight ratio of Na₂O: K₂O used was 5:1 which is more or less of the same order as that recommended by N. I. Lant-s³. In the case of Al₂O₃: B₂O₃, the weight ratio was brought down to as low as 0.06 (*ie*, 1:17.5) resulting in satisfactory acid resistance as well as fusibility. Fluorine was used to the extent of 5.00 parts by weight for good red colour stability⁴. Taking this as starting composition, the effect of variation of TiO₂ and ZrO₂ was studied in respect of fusibility, stability of red colour and acid resistance property and the results are shown in Figs 1 and 2.

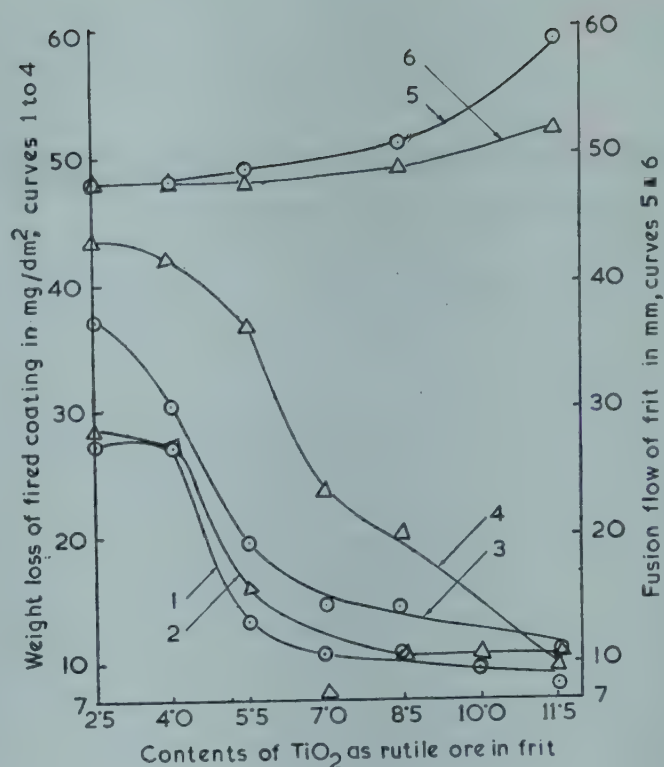


Fig 1

Effect of variation of TiO₂ on fusion flow characteristic of frits and boiling acid resistant characteristic of two base enamels, A (⊙) and B (Δ), both with and without Cd-Se red colouring oxide (4 per cent). 1—enamel A, 2—enamel B, 3—enamel A+colour, 4—enamel B+colour, 5—frit A and 6—frit B

TABLE I
Compositions of transparent base enamel

Melted oxide compositions		Batch compositions		
Constituents	Parts by weight	Raw materials	Parts by weight	
			A	B
SiO ₂	54.00	Quartz	48.5	49.7
Al ₂ O ₃	0.80	Felspar	4.4	4.4
Na ₂ O	12.90	Sodium silicofluoride	8.3	4.7
K ₂ O	2.60	Borax, 10H ₂ O	38.3	38.3
B ₂ O ₃	14.00	Sodium carbonate	6.6	8.6
CaO	3.20	Potassium nitrate	4.3	4.3
F ₂	5.00	Calcium carbonate	5.7	—
TiO ₂	2.50	Fluorspar	—	4.5
		Rutile ore	2.6	2.6
Total	95.00	Total	118.7	117.1

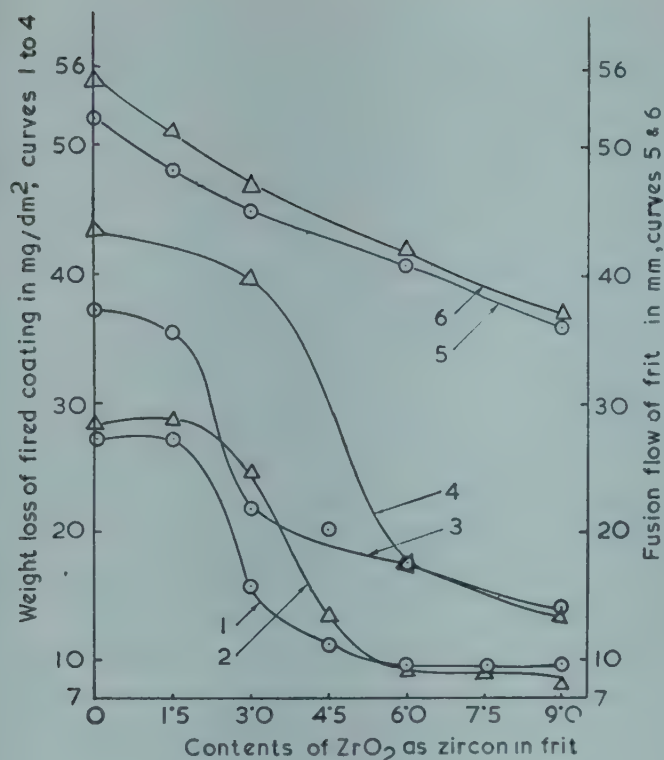


Fig 2

Effect of variation of ZrO_2 on fusion flow characteristic of frits and boiling acid resistant characteristic of two base enamels, A (\odot) and B (\triangle), both with and without Cd-Se red colouring oxide (4 per cent). 1—enamel A, 2—enamel B, 3—enamel A+colour, 4—enamel B+colour, 5—frit A and 6—frit B

Fusion flow studies: On increasing TiO_2 contents, fusibility of the enamel frits remained unchanged (48 mm) up to 4.0 parts of TiO_2 , after which it gradually increased to values (59 and 52 mm) with 11.5 parts of TiO_2 (Fig 1, curves 5 and 6). In case of ZrO_2 (Fig 2, curves 5 and 6), fusibility of the enamel frits uniformly decreased (52 and 55 mm to 36 and 37 mm) with the increase of ZrO_2 from 0.00 to 9.00 parts. This opposite behaviour of TiO_2 and ZrO_2 can perhaps be attributed to their different refractoriness (ZrO_2 —mp 2700° and TiO_2 —mp 2130°) as also to a possible difference in their eutectic forming properties. As regards firing temperature of the base enamels using mill added clay (5 per cent), it was observed that a glossy finish was obtained at 760° . Increase of TiO_2 and ZrO_2 separately in the composition to a maximum of 9.00 parts resulted in the variation of firing temperature

by -20° and $+20^\circ$ respectively. Tables II and III show that the enamels based on batch composition A (using sodium silicofluoride as only the source of fluorine) were slightly more fusible than the enamels based on composition B (using both fluorspar and sodium silicofluoride as sources of fluorine).

Colour stability with Cd-Se red stain: Introduction of Cd-Se red stain (4 per cent) in both types of enamel compositions produced good red colour with the increase of TiO_2 contents up to 8.50 parts, beyond which a gradual discolouration of the red colour to a pinkish brown shade occurred with TiO_2 contents of 11.50 parts. The red colour could not be restored on addition of CdS. Red colour obtained by increasing ZrO_2 content

TABLE II

Comparative study on fusion flow of base frit compositions A and B with variation in TiO_2 contents

Frit compositions	TiO_2 contents in parts by weight	Elongation (mm)
A	2.50	53
B	2.50	51
A-T-1	7.00	53
B-T-1	7.00	52
A-T-2	11.50	59
B-T-2	11.50	56

TABLE III

Comparative study on fusion flow of base frit compositions A and B with addition of varying amounts of ZrO_2

Frit composition	TiO_2 contents in parts by weight	ZrO_2 contents in parts by weight	Elongation (mm)
A	2.50	—	58
B	2.50	—	56
A-Z-1	2.50	4.50	47
B-Z-1	2.50	4.50	46
A-Z-2	2.50	9.00	42
B-Z-2	2.50	9.00	40

in the enamel compositions by more than 6.00 parts was slightly blackish and dense which was comparatively more prominent in the case of composition B. This blackish red colour was probably due to the presence of the selenium resulting from the decomposition of the sulphoselenide compound in the presence of higher ZrO_2 contents. This mechanism of discolouration was confirmed by its restoration on addition of cadmium sulphide in the mill. Subject to these limitations of TiO_2 and ZrO_2 in the compositions it was also found possible to obtain a bright red colour by using only 2 per cent red stain with 1 per cent cadmium sulphide.

Acid resistant property: This property of the coatings with or without red stain as tested by the citric acid spot test method (IS: 3972-1968, 6.1) was observed to be of the highest class (AA) in all the TiO_2 bearing enamel compositions (Tables I and II). In the case of ZrO_2 compositions (Tables I and III), the acid resistant property was somewhat inferior and varied randomly between class AA to class A.

Boiling acid resistant property (ASTM: C-283-1967): Boiling acid resistant property of the TiO_2 bearing base enamel without colour measured in terms of weight loss (Fig 1, curves 1 and 2) shows that the result remained constant up to 4.00 parts of titania. On increasing the TiO_2 content up to 5.50 parts in the base enamel, the weight loss decreases. It shows slight decrease on further increasing the TiO_2 content up to 8.50 parts, beyond which no noticeable change was observed in either of the compositions A or B.

With the introduction of 4 per cent red stain, a sharp increase in weight loss (Fig 1, curves 3 and 4) in comparison with the results obtained for colourless enamels was observed. This was much higher (from 28 mg to 43 mg, *ie*, 15 mg/dm²) in enamels using composition B than that obtained with the enamels using composition A (from 27 mg to 37 mg, *ie*, 10 mg/dm²). The difference in weight loss between transparent and red coloured enamel reached a maximum (21 mg/dm², *ie*, 37-16) with 5.5 parts TiO_2 be-

yond which it sharply declined to zero in the case of composition B with maximum TiO_2 content up to 11.50 parts (Fig 1, curves 2 and 4). The difference in weight loss (Fig 1, curves 1 and 3) between transparent and coloured enamels based on the composition A (with TiO_2 contents varying between 4.00 to 11.50 parts) was almost uniform (about 4 mg/dm²).

In the zirconia bearing base frits, the nature of the weight loss curve on increasing zirconia (Fig 2, curves 1 and 2) was almost similar to that obtained in the case of TiO_2 base frits and weight loss was almost constant (about 9 mg/dm²) on addition of ZrO_2 above 6.00 parts. This observation is also in general agreement with that reported by Turner and Dimbleby².

In the case of red coloured enamels (Fig 2, curves 3 and 4) initial increase in weight loss was appreciable (37.2 and 43.4 mg/dm²) in comparison with the colourless enamels (27.2 and 28.4 mg/dm²) but decreased uniformly (from 10 to 9 and 15 to 9 mg/dm²) on increasing ZrO_2 to 6.00 parts in the enamels A and B respectively. Beyond it both the weight loss curves for coloured enamels using the compositions A and B coincided and continued up to the maximum ZrO_2 content (9.00 parts). The difference in weight loss between transparent and coloured enamels was minimum (about 5 mg/dm²) with ZrO_2 content up to 9.00 parts in the frit. This difference was reduced by 3 to 5 mg/dm² with the use of less quantity of red stain as observed in a few cases.

The increase in weight loss on introduction of red stain in the enamels may be due to the higher solubility of suspended stain particles. The initial high weight loss is considerably reduced by improving the acid resistant property of the enamel by increasing its TiO_2 and ZrO_2 contents. Comparing the behaviour of red coloured (4 per cent red stain) TiO_2 and ZrO_2 enamels regarding weight loss, it was observed that ZrO_2 enamels showed a slightly higher value than TiO_2 enamels. However, the value was practically the same (about 14 mg/dm²) in enamels using ZrO_2 (9.00 parts) as well as those

using TiO_2 (8.50 parts). Random variations in some cases without any definite trend could be attributed to the heterogeneous nature of enamels as well as to the influence of the firing temperature/time schedule and other conditions on their solubility. The relation between the surface condition and the weight loss after treatment with boiling acid was almost similar as described earlier⁵.

Conclusion

Fusibility of the enamel increased with the increase of TiO_2 but decreased with the increase of ZrO_2 . Enamels using fluorine derived from fluorspar were slightly less fusible than those using sodium silicofluoride for the purpose.

Introduction of the cadmium-sulpho-selenide type of red stain in the transparent enamels containing above 8.5 parts of TiO_2 resulted in a gradual discolouration of the red colour to a pinkish brown shade. Effect of red colour in ZrO_2 enamels containing more than 6.00 parts of ZrO_2 showed slightly blackish and dense which was slightly more prominent in the enamels using fluorspar. Blackish tendency of red colour was easily restored by adding a small amount of cadmium sulphide in the mill.

Increase in TiO_2 or ZrO_2 contents in a

transparent enamel did not show any remarkable difference in acid resistant property under spot test conditions, which could perhaps be due to the fact that the test method does not permit finer differentiation between the degrees of acid resistance.

In regard to the boiling acid resistant properties, increase of TiO_2 or ZrO_2 above 6.00 parts in the enamels (originally containing 2.5 parts of TiO_2) had no effect. Addition of Cd-Se type of red stain in the transparent enamels had a significant effect in lowering the boiling acid resistant property. But this tendency due to the introduction of red stain in the enamels could be reduced substantially by increasing the content of TiO_2 or ZrO_2 in the enamels, the former (TiO_2) giving slightly better results.

Both of the original base compositions (A and B) containing 7.5 to 9 per cent TiO_2 or ZrO_2 can be suggested as possible base frits for obtaining coloured enamels possessing acid resistant properties of a high order, in addition to good working properties.

Acknowledgment

The authors thank Shri K. D. Sharma, Director of the Institute, for his kind permission to publish this paper.

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EFFECT OF MINERALISERS ON THE MULLITE FORMATION IN KAOLIN CLAYS

P. S. AGGARWAL, M. K. BANERJEE AND R. V. LELE*

Introduction

Clays, in ceramic products, get converted to mullite on firing. The formation of mullite from kaolinite containing bodies depends upon several factors, *eg*, the firing schedule, duration of soaking at the peak temperature and the presence of mineralisers for reducing the temperature of formation and also to impart special properties like small grain growth. Good quality chemical porcelain was developed at the Institute using mineralisers¹ in china clays. S. P. Chaudhuri² reported the effect of mineralisers for inducing mullitisation in clays which were leached with dilute hydrochloric acid and changed into hydrogen clay. Na₂O and K₂O were the most effective mineralisers for inducing mullitisation. K. J. D. Mackenzie³ made an exhaustive study on the effect of exchangeable cations on halloysite (tubular kaolinite) on the formation of mullite. C. W. Parmelee and A. R. Rodriguez⁴ reported that different oxides added gave different yields of mullite in fired kaolinite. J. Grofcsik⁵, however, reported that mineralisers do not aid mullitisation in fired clays.

M. Slaughter and W. D. Keller⁶ studied the high temperature phases from impure kaolin clays with kaolinite content varying between 15-93 per cent and containing illite and other impurities. It was shown that with increase in illite content in the raw clays the amount of mullite and cristobalite decreased and the amount of glass increased. T. C. Shutt⁷ used

Georgia kaolin for studying the influence of fluorides on the formation of mullite in kaolin. He observed that formation of mullite was aided by the presence of fluoride mineralisers. The firing temperature was 950°. A. J. Shorter⁸ studied the effects of mineralisers on the formation of mullite by refractoriness under load test which gave indirect indication of its formation. Some workers^{9,10,11} have studied the formation of mullite in clay-alumina or silica-alumina mixes. All have reported beneficial effects of mineralisers.

In this communication the results of the effect of mineralisers in inducing mullitisation in different types of kaolinites (ordered and disordered) are reported.

Experimental

All clays except number 4 (Table I) were washed in the laboratory by the usual method:

(i) Rajmahal clay: B.M. Bishui and J. Prasad¹² reported that this was a well crystallised clay. X-ray diffraction examination of the present sample confirmed that the clay was well crystallised one.

(ii) Simultala clay: B.M. Bishui and J. Prasad¹² reported that Simultala clay was a disordered kaolinite. X-ray diffraction examination of the present sample revealed that the clay was disordered type.

(iii) Dwarka Tirumala clay: X-ray diffraction examination showed that this clay was of disordered type. Even after repeated washings and passing through magnet it was not possible to

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remove iron oxide impurities. Isomorphous replacement of iron and aluminium has been reported in disordered type of kaolinites¹³. In such a case it will not be possible to remove iron oxide even after any number of washings.

(iv) Commercial kaolin: Kaolin clay supplied by Bengal Chemical and Pharmaceutical Works was used without any extra processing in this investigation. X-ray diffraction analysis showed that the material consisted of mostly disordered kaolinite and sodium potassium feldspar. No free quartz could be detected by X-ray diffraction or dta. Due to the presence of feldspar, chemical analysis of this clay indicated the presence of alkalis (Table I).

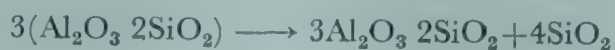
Determination of mullite: Mullite was determined by the chemical method developed by L. L. Vanicheva and S. P. Shmitt-Fogeleovich¹⁴. In this method ground samples of calcined materials were treated with a mixture of HF and HCl for 15 minutes with continuous stirring and the insoluble residue, which was mullite, was weighed. Table II shows the amount of mullite formed from dehydrated clays.

Preparation of samples: LR grade chemicals (Table II) were used as mineralisers in this study. These were mixed with clays by grinding in an agate pestle and mortar using acetone as liquid grinding medium. After drying off the acetone, pellets were pressed under a pressure of

10,000 psi (700 kg/cm²) which were later fired at 1400° for two hours in an electric furnace.

Results

The extent of mullite formation as determined by chemical method, in the presence of different mineralisers, is given in Table II. Mullite is formed from dehydrated clay by the following reaction:



64 gm of mullite would be formed from 100 gm of dehydrated clays. Rajmahal clay and to some extent Simultala clay were nearer to the theoretical analysis of kaolin. Clays 3 and 4 contained excess SiO₂ or excess alkali (Table I) and so naturally mullite content could not be nearer to 64 gm per 100 gm of dehydrated clay in these two clays. It was seen that in a particular type of clay the results were more or less constant. But in the case of 5 per cent Li₂CO₃ as mineralisers the amount of mullite formation was less (Table II). This could be explained due to excess glass formation caused by the fluxing action of lithium carbonate.

Discussion

Kaolinite when heated at 980° started transforming into mullite. In dta, an exothermic peak was observed at this temperature (Fig 1). Early appearance of mullite at the cost of

TABLE I

Chemical analysis of the clays

Clay	Constituents (per cent)								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	LOI
1 Rajmahal	43.62	40.69	0.60	1.06	0.08	Trace	0.06	0.08	13.80
2 Simultala	41.26	42.74	0.27	0.37	0.26	Trace	0.10	0.14	14.80
3 DTM*	56.79	26.53	2.72	1.24	0.60	0.52	1.34	0.43	9.78
4 BCPW†	47.31	32.88	1.96	Trace	1.23	1.93	3.97	0.88	10.14

*Dwarka Tirumala clay; †Kaolin obtained from Bengal Chemical and Pharmaceutical Works

spinel may be shown by smaller dta peaks. At approximately 1200° a second less intense exothermic peak was observed which represented the development of secondary mullite. F. M. Wahl¹⁵ studied the effect of mineralisers on well crystallised kaolinite. He reported that several additives effectively lowered the temperature at which the secondary mullite was formed, whereas some other additives did not have any apparent effect on mullite development.

It was observed from the results that mineralisers added to the clays did not help in increasing the amount of mullite at the firing temperature of 1400°. It is quite possible that the formation of mullite might start at lower temperature under the influence of mineralisers. F. M. Wahl¹⁵ showed that formation of mullite started at lower temperature due to mineralisers, but the amount of mullite formed between 1300° and 1400° was more or less constant with different mineralisers. It is felt that for similar reasons mineralisers in the present experiments also did not aid in increasing the amount of mullite whatever may be the type of kaolinite.

But it is generally believed that mineralisers aid mullite formation. Most of the workers use such starting materials like clay-Al₂O₃ mixtures, Al₂O₃-quartz, silica-alumina gel and acid-

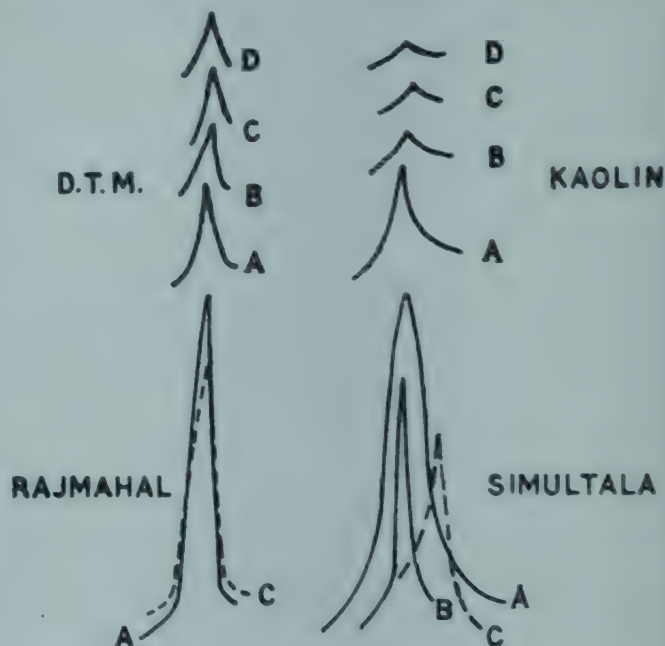


Fig 1

Effect of MgCO₃ in kaolinite type of clays on the exothermic peak. A—as such, B—1% MgCO₃, C—2% MgCO₃, D—5% MgCO₃

TABLE II

Mullite formed by firing the clay with and without mineralisers at 1400° for two hours

Mineraliser	Per cent	Clay 1 Mullite (%)	Mineraliser	Per cent	Clay 2 Mullite (%)	Mineraliser	Per cent	Clay 3 Mullite (%)	Mineraliser	Per cent	Clay 4 Mullite (%)
Nil	—	59.37	Nil	—	51.75	Nil	—	34.20	Nil	—	37.25
CaF ₂	1	55.60	MgCO ₃	1	50.96	CaF ₂	1	33.40	CaF ₂	1	35.00
"	2	55.70	"	2	51.12	"	2	32.32	"	2	33.95
"	5	50.60	"	"	"	"	5	29.02	"	5	30.65
Li ₂ CO ₃	1	57.23	ZnCO ₃	1	51.25	Li ₂ CO ₃	1	33.52	Li ₂ CO ₃	1	34.70
"	2	55.02	"	2	53.02	"	2	30.05	"	2	35.10
"	5	44.65	"	"	"	"	5	23.20	"	5	19.50
MgCO ₃	1	57.15	"	"	"	MgCO ₃	1	36.25	MgCO ₃	1	35.46
"	2	58.15	"	"	"	"	2	35.55	"	2	35.66
"	5	54.05	"	"	"	"	5	34.10	"	5	39.80
AgNO ₃	1	56.07	"	"	"	AgNO ₃	1	35.69	AgNO ₃	0.5	36.50
"	2	56.95	"	"	"	"	2	35.17	"	1	36.83
"	5	56.82	"	"	"	"	5	34.75	"	1.5	36.90
ZnCO ₃	1	60.55	"	"	"	ZnCO ₃	1	36.37	ZnCO ₃	0.5	37.20
"	2	60.38	"	"	"	"	2	36.30	"	1	36.10
"	5	61.22	"	"	"	"	5	37.20	"	2	35.30

Clay 1—Rajmahal clay; Clay 2—Simultala clay; Clay 3—DTM clay; Clay 4—Kaolin from Bengal Chemical and Pharmaceutical Works.

treated clays. It is possible that in such cases, the amount of mullite formation might vary with different mineralisers at particular temperature of heat-treatment.

Differential thermal analysis: Dta of kaolinite shows an exothermic peak at 980°. There is a lot of controversy about this peak. One of the reasons given is that early appearance of mullite shows smaller dta peaks. In the case of Rajmahal clay, mineralisers certainly affect the height of 980° exothermic peak. This shows that nucleation of primary mullite is effected by the presence of mineralisers. Similar results are seen in the case of disordered Simultala clay. In the case of commercial kaolin containing impurities, however, no difference in the height of 980° peak

could be detected, *ie*, in this case mineralisers did not seem to affect the nucleation of primary mullite.

Summary

The effect of mineralisers on the mullite formation in china clays was studied. Four types of ordered and disordered kaolinites were used. It was observed that the mineralisers did not increase the amount of mullite in kaolinites heated at 1400°.

Acknowledgment

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IMPROVEMENT IN BRIGHTNESS OF OFF-COLOURED CERAMIC RAW MATERIALS BY CHEMICAL DECOLOURISATION PROCESS†

S. R. DAS AND S. K. GUHA*

Introduction

Colour of a ceramic material is contributed by the ferruginous impurities present in the clays. Silica, pyrophyllite, bauxite and many other ceramic raw materials are quite often found to contain excess of iron. This restricts their applications in ceramic industries. In case of china clays, it has been shown that the colour of a fired ware is much intensified when titania is associated even with a small quantity of iron oxide¹. Different methods²⁻⁷ were tried to remove iron oxide from clays but most of them proved to be either destructive or were not found to be commercially viable. Iron oxide can be chemically removed resulting in the improvement in brightness of china clays⁸. The results of several laboratory experiments carried out on different ceramic raw materials including clays are presented in this paper.

Experimental

400 gm of the material was taken in a glass beaker, slaked for 2 hours and the volume was so made up with water to allow the suspension to contain about 10 per cent solid. In the case of non-slaking type of material, *eg*, pyrophyllite, bauxite, silica sand, *etc*, they were ground to a desired fineness and then made a uniform suspension by

blunging. The suspension was deflocculated wherever applicable by using suitable dispersing agents. Depending upon the percentage iron oxide present in raw material the suspension was treated with the sodium or zinc salt of hydrosulphurous acid periodically adjusting the hydrogen ion concentration by adding mineral acid. When the desired quantity of chemicals were found to have been consumed as indicated by the stability of pH readings followed by the desired bleaching of the off-colour, the reaction was considered to have been completed. In all the cases, however, the rate of consumption of chemicals was not uniform. A fast rate indicated good amenability and a slow one poor. Such resistance to the progress of chemical reaction was earlier correlated⁸ to the mineral nature of the ferruginous contaminant. The bleached material was then washed with pH controlled water and finally with ordinary water to make it free from excess chemicals. Dry clay was pulverised and discs were pressed. Such discs were examined for their brightness by reflectance measurements before and after bleaching. In all cases a portion of the bleached and unbleached materials were examined for Fe_2O_3 content.

Results and discussion

Table I gives the properties of fourteen clays before and after decolourisation treatment. Clays 1, 2, 10 and 13 (II) which were well below

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grade 2 originally, could be beneficiated to grade 1. Brightness of clay 4 was improved from grade 2 to that of grade 1. Clays 3, 5, 7, 9, 11, 12, 13(I) could also be improved considerably while in other cases brightness could be increased only to a limited extent.

Table II gives the properties of six ceramic raw materials other than clay before and after decolourisation treatment. In these materials improvement in brightness is not a factor for which their uses depend but it is the removal of Fe_2O_3 content which is more important. In sample 1, removal of Fe_2O_3 is not quite satisfactory while in other five samples it is quite appreciable. It is seen from Tables I and II, that those ceramic raw materials which showed none or little resistance to chemical decolourisation increased in

brightness and percentage removal of Fe_2O_3 was also high in their cases. Clays 3 and 9 (Table I) and clay 1 (Table II) showed some resistance to chemical bleaching. Percentage removal of Fe_2O_3 as well as increase in brightness was not at all satisfactory in these cases. This might be due to the presence of organic impurities in the materials serving as protective colloids which inhibited the action of the chemicals.

Conclusion

By using the chemical process developed at Central Glass and Ceramic Research Institute, various ceramic raw materials like clay, bauxite, talc, pyrophyllite and silica sand could be beneficiated resulting either in the improvement in brightness or overall usefulness of the raw

TABLE I

Properties of china clays before and after decolourisation

Serial No	Source	Fe_2O_3 (per cent)		Fe_2O_3 (per cent) removal	Unfired brightness (per cent)		Increase in unfired brightness
		Before bleaching	After bleaching		Before bleaching	After bleaching	
1	Kusumpur, Delhi	2.18	1.33	38.9	68.0	82.3	14.3
2	Cossimbazar pottery grade Bihar	2.39	1.16	51.5	66.0	82.2	16.2
3	Cossimbazar pottery paper, grade, Bihar	2.00	1.90	5.0	70.0	72.2	2.2
4	Travancore	2.06	1.59	22.8	77.1	83.0	5.9
5	Bankura, West Bengal	1.03	0.50	51.4	69.2	78.5	9.3
6	Colombo, Srilanka	1.26	0.70	44.3	61.1	64.5	3.4
7	Rajasthan	9.76	0.46	95.3	HC	79.2	—
8	Modinagar, Rajasthan	2.62	1.39	35.5	65.1	73.3	8.2
9	Birbhum, West Bengal	1.44	1.28	11.1	72.9	78.3	5.4
10	Kurma, Orissa	2.41	1.74	27.8	70.0	82.0	12.0
11	Dalmianagar, Orissa	2.18	0.98	55.5	64.2	77.5	13.3
12	Lohardanga, Bihar	1.12	ND	—	71.0	78.5	7.5
13	Orissa (I)	3.33	ND	—	70.3	79.4	9.1
	„ (II)	3.59	ND	—	65.2	81.0	15.8
14	Pappinisseri, Kerala	1.02	ND	—	67.0	70.0	3.0

HC—highly coloured; ND—not determined

TABLE II

Percentage of Fe_2O_3 removal after decolourisation

Serial No	Sample	Source	Fe_2O_3 (per cent)		Fe_2O_3 (per cent) removal
			Before bleaching	After bleaching	
1	Talc	Jabalpur, MP	0.59	0.50	15.3
2	Fire clay	Palamau, Bihar	0.67	0.39	41.8
3	Bauxite	Shavroy, Madras	3.17	1.58	50.1
4	Bauxite	Katni, MP	2.20	1.44	34.5
5	Pyrophyllite	Uttarpradesh	3.45	1.96	41.7
6	Diaspore	Jhansi, UP	3.26	1.11	65.9

material in the relevant industries.

Summary

Ferruginous impurities contribute largely to the colour of ceramic materials. This colour is intensified in the fired state when titania is associated even with a small quantity of iron oxide. By the process of chemical bleaching developed at the Institute, these contaminants could be reduced. This makes the raw materials more useful for ceramic industries.

Several samples including clay, pyrophyllite,

bauxite, silica sand from India were studied and improvement in brightness was achieved by chemical decolourisation process of ceramic raw materials. Reduction in percentage of Fe_2O_3 in most of the minerals and improvement in the brightness could be achieved by this process.

Acknowledgment

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THERMOLUMINESCENCE RESPONSE OF QUARTZ AND SOME SILICATE GLASSES TO GAMMA RAYS AND UV RADIATIONS

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Introduction

Influence of impurities on the radiation effect on quartz and complex silicate glasses has been recognised by many workers¹⁻⁷. Materials which have not been purified, form absorption bands under ionising radiation, however, extremely purified fused silica shows no change in their absorption^{4,8}. Alkalies, aluminium and germanium are the impurities which might be present in silica. Several authors studied the effect caused by germanium^{1,9,10} and aluminium^{11,12}. J. R. Hensler¹³ studied the thermoluminescence (TL) of silica powder doped with aluminium in combination with other ions and found an interaction of these ions with the silica network.

Natural sands had been studied by some authors^{14,15} as a material for dosimetry by using the TL property of the sands. In the present study the effect of γ -rays and uv radiation on the TL of quartz is reported. The effect of the presence of significant amount of alkalies in the SiO_2 network on TL is investigated. The effect of electromagnetic radiations on the TL response of soda-lime-silica glass doped with Cu^+ ions is reported.

Experimental

Materials preparation: Compositions of specimens used in this study are reported in Table I. Natural quartz was used as a source for SiO_2 . The glasses were made from powdered natural quartz and AR grade chemicals. Glass batches

were melted in pt-rhodium crucibles at 1450° for 3 hours. The glass doped with Cu^+ ions was prepared by melting the batch composition by adding CuO and oxalic acid. The amount of oxalic acid to be added was determined experimentally so that the glass was colourless.

For measuring the TL response, the glass specimens and quartz were ground in agate mortar and used in the powdered form after passing through a sieve of 160 mesh. Specimens 5a and 5b were used as slabs of 1 mm thick.

Irradiation facilities: Two sources for γ -rays were used. Cs^{137} γ -ray source was used for absorption rate of 0.75 rad/min and Co^{60} γ -ray source for 0.12 Mrad/hour. A 3.7 kW mercury lamp was used as a source for uv radiation. The samples were placed at 30 cm from the lamp and irradiated for 30–60 secs.

TL read out unit: TL measurements were recorded by the Harshaw 2000 A+B system and the glow curves were drawn on X-Y recorder. The maximum tray temperature was 400° for a heating cycle of 60 secs. TL yield was recorded in nanocoulomb (nc). Unless specified, quartz and glasses were counted 24 hours after the end of irradiation processes.

Results

The effect of introducing Na_2O into the SiO_2 network was studied in samples 2, 3 and 4. Table II shows the TL yield of these samples and their structural characteristics¹⁶. It can be noticed that an increase in the number of molecules of Na_2O , decreases the TL yield (Fig 1). Fig 2 shows this effect on the glow curves

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of the specimens studied. There are two glow peaks in the glow curve of quartz; the first at about 136° and the second at about 285°. Similar two peaks are observed in specimen 2 at about 128° and 292°. The latter peak was of very low intensity. The increase of the Na₂O content in samples 3 and 4 was accompanied by a disappearance of the high temperature glow peaks and a decrease in the intensity of the low temperature glow peaks observed in samples 1 and 2. For sample 4, a glow peak at 170° was observed in addition to the lower temperature glow peak which can be observed around 100° (Fig 2).

TL yield of natural quartz due to the action of γ -rays and uv radiations are given in Table III. A noticeable increase in the TL yield from 0.02 nc/mg to 218.18 nc/mg was seen as the absorbed dose increased from 4 rad to 10⁴ rad. When the absorbed dose increased to 0.12 Mrad, small increase in the TL yield (about 31.67 nc/mg) was recorded indicating that a saturation condition might have been reached. The uv radiation has little or no effect on the natural quartz as the TL yield recorded is too small (about 0.004 nc/mg). Specimen 5b (Table III) was sensitive to both γ -rays and uv radiations as compared with 5a. Increase in the γ -rays, absorbed dose up to 0.18 Mrad increased the TL to about 1668.27 nc/mg before saturation effect as that observed at 0.12 Mrad in natural

TABLE I
Chemical analysis of the clays

Sample	Composition (mole per cent)		
	SiO ₂	Na ₂ O	CaO
1	100.00	—	—
2	73.69	26.31	—
3	64.22	35.78	—
4	60.34	39.66	—
5a	62.40	16.69	20.91
5b*	62.40	16.69	20.91 + 0.1 gm CuO / 100 gm glass

*11 gm oxalic acid, 100 gm glass were added as a reducing agent

quartz. In specimen 5a, γ -rays absorbed dose of 0.12 Mrad gave a TL yield of about 9.05 nc/mg. Increasing the absorbed dose to 0.18 Mrad gave the TL yield of 22.47 nc/mg.

Cuprous ions increased the sensitivity of soda-lime silica glass to uv radiations. For irradiations of 30 secs, specimen 5b gave TL yield of 85.24 nc/mg; while the yield was 35.00 nc/mg for 150 secs irradiation of specimen 5a.

TL yield due to uv radiations on the specimen 5b was too large to be compared with that of

TABLE II

Mullite formed by firing the clays with and without mineralisers at 1400° for 2 hours

Sample	TL yield (nc mg) after 0.12 Mrad	Approximate proportions of SiO ₂ groups linked into glass structure by			Remarks*
		4 bonds	3 bonds	2 bonds	
1	250.0	100	—	—	
2	15.9	30	70	—	2.5 Na ₂ O, 0.7 SiO ₂
3	9.9	—	90	10	3.9 Na ₂ O, 0.7 SiO ₂
4	2.7	—	70	30	4.6 Na ₂ O, 0.7 SiO ₂

*From reference 16

natural quartz. Fig 3 shows the glow curves of the specimens 5a and 5b after being irradiated with Co^{60} γ -ray for one hour. Cu^+ containing glass (specimen 5b) showed one symmetrical broad band with peak at 228° while an unsymmetrical band of lesser intensity was observed at 336° for the specimen 5a which contained no Cu^+ ion.

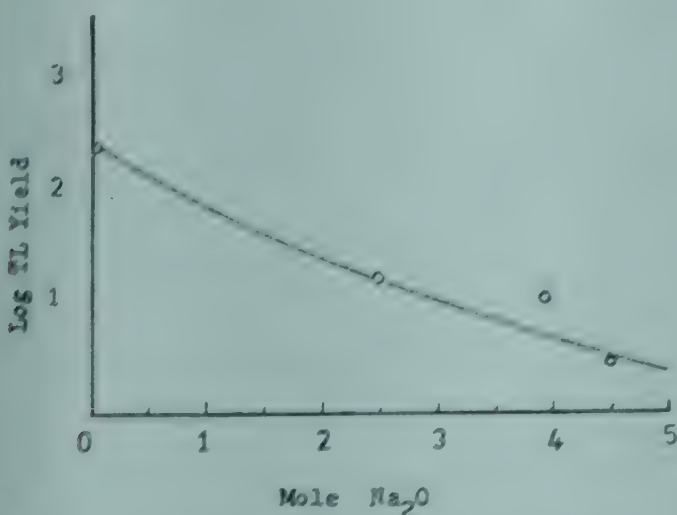


Fig 1
Effect of increasing Na_2O content on the TL yield of sodium silicate glasses after exposure to 0.12 Mrad. Quartz represents samples containing zero mole Na_2O

TABLE III

TL response of quartz and glasses undoped and doped with Cu^+ ions to γ -ray and uv radiations

γ -ray absorbed dose (rad)	TL yield (nc/mg) of sample		
	1	5b	5a
4	0.02		
47.5	0.39	0.04	
176	1.02		
890	15.05	4.13	
3300	77.31	11.06	
10^4	218.18	48.27	
12×10^4	249.81	441.01	9.05
18×10^4		1668.27	22.47
uv	60 sec 0.004	30 sec 85.24	60 sec 14.68
		60 sec 192.02	150 sec 35.00

Discussion

The result reveals that natural quartz has TL response to γ -rays, especially for low doses. The TL response of soda-silica glasses decreased with increase in the Na_2O content. The TL response of soda-lime-silica glass was only for high doses of γ -rays and uv radiation. Doping of the glass with Cu^+ ions rendered it sensitive to both low and high doses of γ -rays or uv radiations.

The appearance of two glow peaks in the glow curve of quartz, at 136° and 285° , may be attributed to the presence of impurities, mainly aluminium. This is in good agreement with the results obtained by E. Lell⁵. Fig 4 shows two glow curves obtained by him in which fused silica showed one peak at 120° while fused silica doped with 0.2 per cent Li and 2.0 per cent Al showed two glow peaks at about 88° and 310° . The glow curve of quartz studied by R. Yokota¹⁷, also showed two glow peaks. The peak at lower temperature was

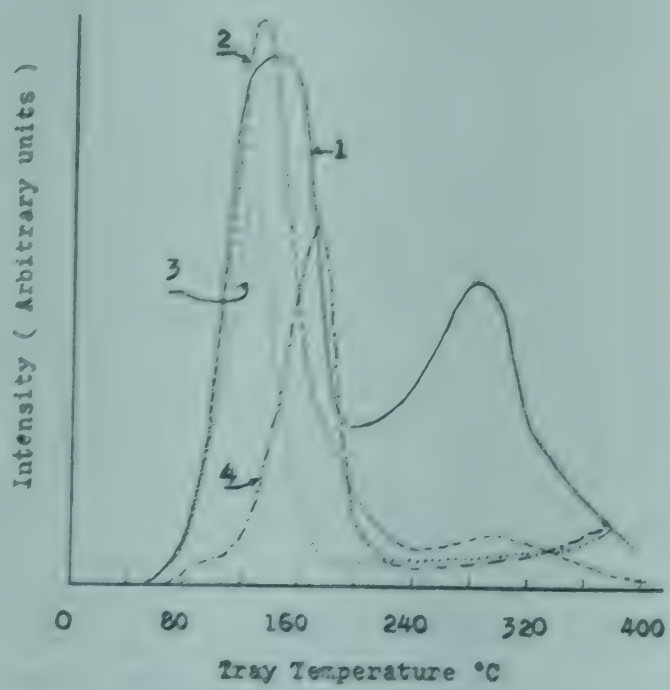


Fig 2
Thermoluminescence of quartz (curve 1) and sodium silicate glasses of varying Na_2O content (curves 2 to 4) after exposure to 0.12 Mrad. The intensity of the glow (curve 1) is much higher than the others

split into two at about 150° and 200°, and the high temperature peak was at about 300°.

The high temperature glow peak of samples 1 and 2 (Fig 2) was associated with centres formed in defects present in the SiO₂ network. The change in the composition from samples 1-4 was accompanied by a decrease in the intensity of the glow peak which might be attributed to the decrease of the probability of such defect to be formed in the structure of glass.

The low temperature glow peak at 100-136° (Fig 2) may be associated with centres formed in bridging oxygen vacancies which absorb at 2.2 eV. The increase of alkali leads to the formation of non-bridging oxygen (glass 5, Table II). Consequently non bridging oxygen vacancies will be formed with greater probability than bridging oxygen vacancies during irradiation. These defects trap electrons and complex centres may be formed^{1,18}, eg, Me^{T3-}, Al_B⁻ and Na^{D-} centres. The thermal excitation of electrons of such centres may result in the formation of the glow peaks observed at 100-136° and 170°.

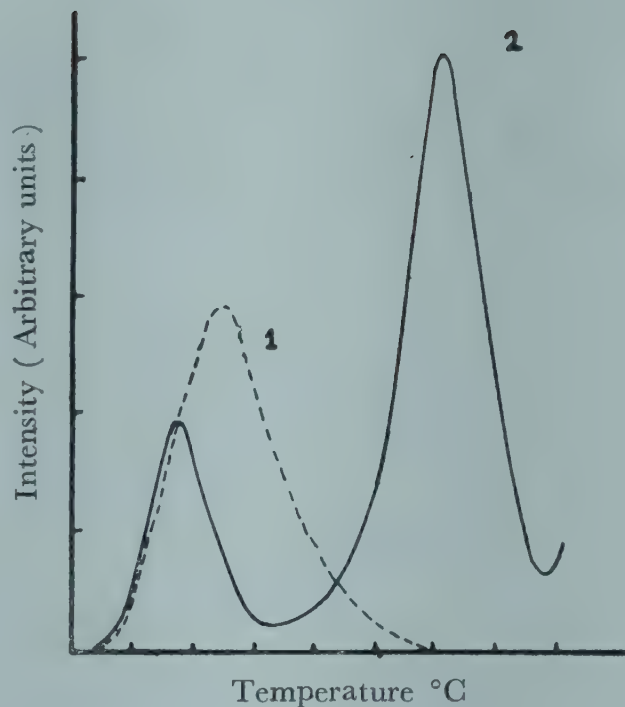


Fig 4
Thermoluminescence of undoped fused silica (curve 1) and fused silica doped with 0.2 per cent Li and 2.0 per cent Al (curve 2). Heating rate used was 0.50/sec (from reference 16)

During the irradiation of glass 5b, the reaction $\text{Cu}^+ + h\nu = \text{Cu}^{2+} + e$, might take place. Consequently the probability for formation of colour centres in the oxygen vacancies or a trapped metal ion (Me^{D-}) will increase. Metastable copper atoms Cu^{+D-} may be formed in such glasses¹⁹. The release of electrons from these centres and some others may result in the glow peak at 228°.

The absence of 228° glow peak in specimen 5a is a confirmation for the role of Cu⁺ ions in the formation of luminescence centres responsible for the glow peak at 228°. The glow peak observed in specimen 5a at 336° may be attributed to the formation of colour centres that absorb in the uv region²⁰ which may be thermally bleached around 336°.

Conclusion

Natural quartz may be recommended to be used as a tool for measuring the low losses of

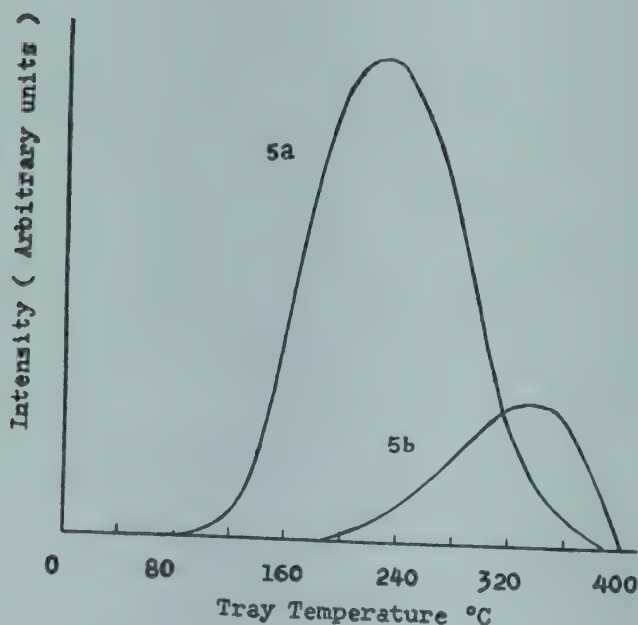


Fig 3
Thermoluminescence of undoped soda-lime-silica glass (curve 5a) and soda-lime-silica glass (curve 5b) doped with cuprous ions after exposure to 0.12 Mrad

γ -rays (below 0.12 Mrad) while soda-lime-silica glass may be recommended for the high doses (about 0.12 Mrad).

Cu^+ ions when present in soda-lime-silica glass increase the TL response to γ -rays and uv radiations and can be recommended to be used for measuring both the low and high doses of radiations. Natural quartz may show two glow peaks at 136° and 285° due to presence of impurities, mainly Al. This glow may be attributed to release of electrons from Al_B -centres and centres involving Si-O vacancies.

Soda-silica glasses might show glow peak either in the region 100-136° or at 170° according to the SiO_2 content. Soda-lime-silica glass showed glow peak at about 336°, while that doped with Cu^+ ions showed one glow peak at about 228°. The low temperature glow peaks at 100-136°, 170° or 228° might be attributed to release of electrons from $\text{Me}^{\text{T}3-}$, Al_B -, or $\text{Me}^{\text{P}-}$. The glow peak at 336° may be assigned to release of electrons from colour centres that have

absorption peaks in the uv region.

The relation between absorption centres and luminescence is not a simple one.

Summary

Thermoluminescence (TL) response of natural quartz, soda-lime-silica glasses with and without Cu^+ ions to γ -rays and uv radiations were investigated. Natural quartz was found to have good TL response to the low γ -ray doses, which shows thermoluminescence peaks at 136° and 285°. This may be due to release of electrons from Al_B -centres involving Si-O vacancies. Soda-silica glasses show one glow peak either at 100-128° or at 170° which may be assigned to bleaching of Al_B - and $\text{Me}^{\text{T}3-}$ or $\text{Na}^{\text{P}-}$ -centres.

The increase of Na_2O content decreased the TL response of soda-silicate glasses to γ -rays. Doping of soda-lime glasses with Cu^+ ions increased greatly its TL response to both low and high doses of γ -rays and uv radiations.

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MICROINDENTATION HARDNESS OF GLASSES: PART I— CABAL GLASSES

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Introduction

M. Prod'homme¹ investigated the relationship between the microhardness and viscosity to support the idea that microhardness can be considered within limitations, as a typical property of glass strength.

R. Van Laetham² pointed out that hardness values depended upon the instrumentation and the technical procedure used. For this reason Vickers hardness tests were carried out keeping the geometrical factors of the indenter identical whatever the instrument used. Identical Vickers

indenter gave results reproducible with an accuracy of ± 3 per cent.

The phenomenon of microhardness indentation needs to be correlated not only to any single property such as strength but also with viscous flow, compaction and local heating. Lubrication effect seems also to be involved³. In the present communication Vickers hardness of cabal glasses is presented.

Experimental

Measurements: The samples were prepared in the shape of small plane parallel plates approximately $50 \times 10 \times 4$ mm. All samples were well

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ground and finely polished from one side until they exhibited a faultless surface.

The samples were mounted on the objective stage of the Carl Zeiss Microhardness Tester and brought into focus of the viewfinder objective (magnification $\times 10$). The part of the specimen suitable for indentation was put at the centre of the field of view. The measuring objective (magnification $\times 40$) was then engaged and the focus was adjusted. The indenter was set at its starting position and then released by a trigger. Under a load up to 100 gm the indenter penetrated slowly into the glass for 10 seconds. Then it was raised. After removing the indenter the measuring objective was used to measure directly the value of the diagonal of the impression in the measuring eye piece with an accuracy of about 1/10 of a micron.

The diamond-shaped indentation was measured with an estimated accuracy of ± 0.5 μ m. At least ten indentations were made and measured for each sample. After the first five measurements, the sample was repositioned and the remaining five indentations were made in a new area.

After the indenter had completed its descent, it was allowed to remain on the sample for 10 seconds before being raised. Testing with loads up to 100 gm could be used without causing microcracks to emanate from the indentations. This was recently recommended by M. Wada *et al*⁴. These tests were never taken near the edge of a sample or any closer than three times the diameter of an existing impression. The Vickers hardness, H , (tetragonal pyramid) corresponding to an impression of diameter (diagonal) d , was calculated from equation 1:

$$H = 1854.4 (P/d^2) \text{ kg/mm}^2 \quad \dots (1)$$

where P , the load was expressed in gm and d in microns.

Results

The glass compositions investigated and the results obtained are tabulated in Tables I to IV.

Influence of the composition of glass: Introducing any of the monovalent alkali oxides in place of

CaO decreased the microhardness number. The effect was greatest in the glasses containing lithia, and least in glasses containing potash, with the glasses containing sodium having intermediate values (Table I).

The replacement of lime by a divalent metal oxide decreased the microhardness number in the case of CdO, SrO, BaO and increased the values in the case of MgO or ZnO (Tables II and III).

The tetravalent metal oxides increased the microhardness number (Table IV) in the order zirconia, titania, silica when replacing boric oxide. These results were parallel with the littleton softening points of these glasses published before⁵.

Hardness as a function of load: The microhardness of four glass compositions was investigated as a function of the applied load. The results are given in Table V. The log d plotted against log p derived from these data gave straight lines with an approximately identical slope. The results indicated that the Vickers microhardness increased with the decrease of the load.

Discussions

Glass behaves like a brittle material when it is loaded and its hardness is measured as a residual impression of the penetration after the load has been removed. This view of brittleness of glass is not universally endorsed. Arguments have been advanced that glass deforms plastically under sufficiently high stress.

The mode of deformation in ceramic materials is highly dependent on the structure. In glass, the lack of any long range order makes dislocation motion to be impossible. However, these materials can deform by viscous process under proper conditions of stress and temperature.

A good correlation between the hardness and the temperature at which the viscosity is 10^{11} poise was established by R. E. Bastick⁶. He suggested that the glass temperature rises to such a value in the neighbourhood of the diamond apex that truly viscous flow occurred.

R. W. Douglas⁷ argued that a flow or plastic

yield of the glass takes place at room temperature when the loaded diamond point touches the surface. The viscosity of the glass under the intense load is sufficiently reduced to allow flow to take place. He added that it would have been preferable to plot the indentation hardness results against the temperature at which the viscosity is 10^{14} as this would approximate more closely to the fictive temperature of glasses subjected to the normal annealing processes.

W. A. Weyl and E. C. Marboe⁸ described the effect of shear stresses as a disproportionation of the binding forces and the ability of the system to flow because of the weaker forces. For all flow processes the polarisability of all ions was of paramount importance.

D. M. Marsh⁹ assumed that the Vickers diamond hardness impression on glass was indi-

cative of plastic deformation. The plasticity was enhanced due to environmental factors such as the softening of the glass by adsorbed water vapour or built in water. Frictional heating may be sufficient to soften the lower melting glasses.

M. Goldstein¹⁰ developed a theory of cold flow in polymers which could explain the diamond pyramid hardness behaviour.

M. Prod'homme¹ suggested that the microhardness and viscosity are related. In order to support this idea an optical glass was studied at various heat-treatment temperatures. The glasses with a weakly bonded molecular structure had lower Vickers microhardness number and the value increased with the compactness of the glassy network.

Two ways of frozen viscoelastic deformations were proposed by G. M. Bartenev *et al*¹¹:

TABLE I

Vickers hardness of cabal glasses containing Li_2O , Na_2O , K_2O as replacement for CaO

Glass	Glass composition (wt per cent)				Vickers number† DPH (kg/mm ²)	Softening point (°C)
	CaO	B ₂ O ₃	Al ₂ O ₃	R ₂ O*		
1	30	40	30	Li ₂ O 1 5 10 15 20 25 30	720	694
2	29	40	30		681	693
3	25	40	30		662	667
4	20	40	30		640	641
5	15	40	30		623	620
6	10	40	30		602	588
7	5	40	30		589	561
8	—	40	30		571	550
9	29	40	30	Na ₂ O 1 5 10 15 20 25 30	690	694
10	25	40	30		672	673
11	20	40	30		648	648
12	15	40	30		627	627
13	10	40	30		611	593
14	5	40	30		592	566
15	—	40	30		580	555
16	29	40	30	K ₂ O 1 5 10 15 20 25 30	694	694
17	25	40	30		678	680
18	20	40	30		655	651
19	15	40	30		639	634
20	10	40	30		616	598
21	5	40	30		596	569
22	—	40	30		586	559

*All replacements are made on the cation for cation basis; †Under the load of 80 gm

TABLE II

Vickers hardness of cabal glasses containing MgO, ZnO, CdO as replacement for CaO

Glass	Glass composition (wt per cent)				Vickers number* DPH (kg/mm ²)	Softening point (°C)
	CaO	B ₂ O ₃	Al ₂ O ₃	RO		
				MgO		
23	29	40	30	1	724	694
24	25	40	30	5	727	698
25	20	40	30	10	731	705
26	15	40	30	15	739	711
27	10	40	30	20	743	718
28	5	40	30	25	750	725
29	—	40	30	30	755	735
				ZnO		
30	29	40	30	1	722	694
31	25	40	30	5	726	697
32	20	40	30	10	730	703
				CdO		
33	29	40	30	1	712	682
34	25	40	30	5	694	674
35	20	40	30	10	680	666
36	15	40	30	15	665	657
37	10	40	30	20	648	647
38	5	40	30	25	630	638
39	—	40	30	30	612	627

*Under the load of 80 gm

TABLE III

Vickers hardness of cabal glasses containing SrO, BaO as replacement for CaO

Glass	Glass composition (wt per cent)				Vickers number* DPH (kg/mm ²)	Softening point (°C)
	CaO	B ₂ O ₃	Al ₂ O ₃	RO		
				SrO		
40	29	40	30	1	710	—
41	25	40	30	5	683	—
42	20	40	30	10	669	—
43	15	40	30	15	646	—
44	10	40	30	20	622	—
45	5	40	30	25	601	—
46	—	40	30	30	583	—
				BaO		
47	29	40	30	1	708	682
48	25	40	30	5	677	672
49	20	40	30	10	656	662
50	15	40	30	15	638	650
51	10	40	30	20	613	635
52	5	40	30	25	590	625
53	—	40	30	30	577	615

*Under the load of 80 gm

(i) high stress elastic deformation of the glassy network when only the shape but not the volume of the glass changes, and (ii) three dimensional deformation of the glass, when the loose structural network becomes compacted.

From indentation experiments on glasses K. W. Peter¹² concluded that: (i) all glasses could be compacted, (ii) the pressure on the area of indentation was constant within a wide range, and (iii) the flow properties were correlated to a minimum percentage of network modifiers.

The modes of deformation were summarised by A. R. C. Westwood and R. D. Huntington¹³ as follows: (a) flow in amorphous solids may involve the motion of dislocations of variable Burger vectors as suggested by J. J. Gilman¹⁴, (b) mobile bond weakening sodium ions played important role in facilitating flow^{15,16}, and (c) mobile OH⁻ ions were involved in the flow process. Their migration near to the surface layer was responsible for the observed softening¹⁷. G. J. Copley¹⁸ defined plastic flow as essentially a reconstructive change involving bond exchange. F. M. Ernsberger¹⁹ added that the

primary interatomic bonds were broken and reformed with a series of new partners as was required to provide for inelastic deformation in shear, volume remained constant, and the deformation was not recoverable upon heating.

J. J. Gilman²⁰ described the dislocation lines with variable Burger vectors which could exist in glasses with no definite slide planes so that appropriate driving shear stress was simply the maximum applied shear stress which equalled half the applied tension or compression in a uniaxial test. When multiaxial stresses were present, the root mean square or octahedral shear stress was the appropriate driving stress. J. J. Gilman²⁰ also added that silicate glasses tended to be viscous, while metallic glasses tended to be plastic, and amorphous polymers lay somewhere in between.

G. M. Bartenev *et al*²¹ assumed that the mechanism of inorganic glass deformation during microindentation was carried out by two stress relaxation processes. The first stage was associated with elastic deformation of the glass network without rupture of the chemical bonds, while the second stage was associated

TABLE IV

Vickers hardness of cabal glasses containing SiO₂, TiO₂ and ZrO₂ as replacement for B₂O₃

Glass	Glass composition (wt per cent)				Vickers number* DPH (kg/mm ²)	Softening point (°C)
	CaO	B ₂ O ₃	Al ₂ O ₃	RO ₂		
				SiO ₂		
54	30	39	30	1	728	694
55	30	35	30	5	738	700
56	30	30	30	10	766	712
57	30	25	30	15	787	727
58	30	20	30	20	810	758
59	30	15	30	25	863	794
				TiO ₂		
60	30	39	30	1	724	694
61	30	38	30	2	728	695
62	30	35	30	5	736	702
				ZrO ₂		
63	30	39.5	30	0.5	722	694
64	30	39	30	1	724	694
65	30	38	30	2	727	697

*Under the load of 80 gm

with diffusion of sodium ions at room temperature or with diffusion of oxygen ions at 100° to 200°.

It was probable that the slip which takes place was non-crystallographic²² and the mechanism of hydrolytic weakening took place *via* the migration of hydrogen-bonded Si-O links.

T. Izumitani and I. Suzuki²³ claimed that the indentations formed in optical glasses containing a large amount of modifiers were due more to plastic flow than to densification.

I. Yasui and M. Imaoka²⁴ refer the cause of the indentation due to microplasticity.

Densification: Several authors²⁵⁻²⁹ have shown that some physical properties of glass, *eg*, density

and refractive index undergo unrecoverable changes upon subjecting the glass to high pressure. This densification may be due²⁷ to the possibility of entanglement of parts of the network. An alternative explanation is that compaction is the main deformation mechanism, but that two relaxation mechanisms operate: (i) one leads to geometric recovery, and (ii) the other to a relaxation of the structure so as to restore the normal properties but locking in the distorted shape.

F. M. Ernsberger assumed³⁰ that plastic flow requires deformation in shear, which necessarily involves the breaking of interatomic bonds and the formation of new bonds with new partners. This is not so in glasses and that microplastic effects are produced by densification. The permanent densification anomaly were discussed³¹ by assuming that the low coordination number of silicon prevented the formation of close-packed arrangements. However, the space remained potentially available and the application of hydrostatic pressure must ultimately force the small shift of atomic position and the small rotation and flexures of bonds that permit an overall decrease in volume of the system. In other words, densification was displacive transformation, while plastic flow was reconstructive.

W. B. Hillig³² claimed that the hardness measurements could be understood in terms of densification or inelastic behaviour, and when pile-up of material occurred it could be attributed to frictional heating. Also there were several arguments about the possibility of dislocation in glassy structures^{33,34}.

J. E. Neely and J. D. Mackenzie³⁵ have shown that it is likely that the displacement of glass is a bulk property rather than a surface controlled phenomenon. The mechanism of densification is expected to be the cause of the indentation. J. D. Mackenzie and S. Saaka³⁶ suggested that the most important observation was the partial recovery of the indentation at much lower temperature than the glass transition temperature, T_g . This kind of recovery could not be easily explained if plastic or viscous flow

TABLE V

Vickers hardness of cabal glasses with different loads

Glass	Load (gm)	Vickers number DPH (kg/mm ²)
1	22	944
	45	866
	70	790
	80	720
	92	700
	116	686
6	22	890
	45	804
	70	703
	80	602
	92	686
	116	570
9	22	943
	45	674
	70	760
	80	690
	92	680
	116	673
24	22	946
	45	883
	70	808
	80	727
	92	703
	116	694
25	22	955
	45	872
	70	811
	80	731
	92	706
	116	700

was assumed to have taken place at the time of indentation.

D. R. Uhlmann³⁷ observed a pronounced maximum in densification studies of alkali silicate glasses in the vicinity of 10 mole per cent alkali oxide. These maxima are taken to reflect a competition between two processes, one of which—the variation of molecular mobility with composition—should lead to increasing densification with increasing alkali concentration. D. R. Stewart *et al*³⁸ investigated $\text{Na}_2\text{O-B}_2\text{O}_3$ and $\text{K}_2\text{O-B}_2\text{O}_3$ system. The densification in these glasses was associated with a decrease in void space in the glasses due to a filling effect of ions. These interpretations are, however, complicated by the changes in boron coordination from triangles to tetrahedra which occur over the composition ranges studied.

D. R. Uhlmann³⁷ suggested that fused silica and other network-based oxide glasses could accommodate the application of pressure by propagating slight distortions of bond angles and geometrical rearrangements throughout the structure. These changes in configuration were readily frozen in. With increasing alkali oxide concentration, rearrangement by rotations about bonds and by local slip should become more prevalent. These distortions were more localised and should be more readily relieved when the pressure was released. Phase separation has been shown³⁹⁻⁴¹ to be contributing to a decrease in densification.

Environment sensitive effects: The anomalous indentation creep of non-metallic solids and glasses was shown⁴² to be due to the presence of adsorbed water.

A. R. C. Westwood⁴³ advanced the following possibilities for the adsorption-induced variation in the hardness of glasses and ceramics: (a) reduction in the surface free energy of the solid (rebinder effect), (b) adsorbed species relaxes surface stresses, *ie*, surface tension force, by causing some localised rearrangement of the atoms and variation in the lattice parameter at the surface, thus affecting dislocation mobility, and (c) adsorption-induced changes in the nature

of the charge of the double layer.

A. R. C. Westwood *et al*^{44,45} believed that the hardness of the near-surface regions of glass will be dependent on the weakening influence of mobile sodium ions¹⁶ and the dislocation-like defects involved in the flow or fracture behaviour of glasses. With regard to flow, there is convincing evidence by some authors^{15,9,46,47} that it can occur in glasses at appropriate temperature.

It has been assumed^{34,48} that the mobile OH^- ions are responsible for the softening of the glass surfaces.

S. M. Cox¹⁶ gave an account of strength behaviour in glasses by ascribing to mobile (sodium) ions a local bond weakening influence due to elastic strain when they occupied interstitial sites. Rupture was initiated by the probability that a number of such ions cooperated to initiate a self generating flow.

Rheological considerations showed^{49,50} that in the presence of network modifiers potential barriers of various heights occurred. When flow occurs, groups of atoms start moving. The atoms are strongly bound to each other within the groups, but only loosely bound to their surroundings with the exception of one atom. At this state a local stress concentration is generated providing the energy for the motion. The microhardness of soda lime glass and of non-metallic solids were found⁵¹ to be maximum when their surfaces are uncharged, *ie*, when they are at zero point of charge as indicated by ϵ -potential measurements.

Relation of microindentation hardness to glass composition: L. Ainsworth⁵² showed that the flow of glass is directly related to the proportion of network modifiers introduced into the structure, the hardness decreased rapidly as network modifier was added. The addition of network modifiers introduced non-bridging atoms into an otherwise complete network. Thus it was reasonable to suggest that flow was facilitated by having a large number of non-bridging atoms which are 'loose ends' in the structure and permit flow in a manner somewhat analogous to

the half-planes which terminate on dislocations in crystals. The addition of alkali to silica weakens the structure by breaking Si-O-Si bonds. The combination of two alkalis permits a more efficient packing and thus produces a maximum diamond pyramid hardness (DPH) for a certain $K_2O:Na_2O$ ratio. Alkali ions introduce polarisable O^{2-} ions that disproportionate the binding forces into some stronger and some weaker forces, increasing the polarisability of all O^{2-} ions. K_2O is more effective than Na_2O with respect to both changes. The gradual replacement of Na_2O by CaO increases the DPH. This is explained on the basis that the Ca^{2+} ions coordinate with the highly polarisable non-bridging O^{2-} ions. This means that the highly polarisable O^{2-} ions are eliminated when Ca^{2+} ions are introduced. L. Ainsworth⁵² arranged the relative effect of the divalent oxides upon the decrease of the hardness as follows: CaO , SrO , BaO , ZnO , MgO , PbO .

R. W. Douglas⁷ showed that indentation hardness can be correlated with the structure of glass and with variations in composition. This indicated a change in the viscosity or softening parameters of the glass. This goes with a previous assumption by H. E. Powell and F. W. Preston⁵³ that the hardness is a property that may be closely related to the mechanical strength of glass and to its low temperature viscosity.

The work of F. C. Eversteijn *et al*⁵⁴ on the hardness of $Na_2O-B_2O_3$ glasses with varying Na_2O content showed a maximum at a composition containing about 25 wt per cent Na_2O in the quenched glasses and a broad range in the annealed glasses. They interpret this anomaly as indicating that there is a relationship between viscosity and hardness for the given types of glasses.

A. Petzold *et al*⁵⁵ correlated the indentation hardness of systematically varied glass compositions with their molar refractivities, the polarisabilities of the cations and with the softening temperatures of the glasses.

W. A. Weyl and E. C. Marboe⁸ assumed that the hardness was initiated by cations of low

polarisability. A relation existed between the hardness and the energy requirement for temporarily unscreening of cations or positive cores and for overcoming the repulsive forces between incompletely screened cations.

A. N. Georoff and C. L. Babcock⁵⁶ observed that the hardness number of some silicate glasses were linearly related to oxide compositions expressed in mole fraction. Evaluations of the data indicated that these linear relations were unique for each of the primary crystallisation phase field of the glasses studied.

Hardness and glass microstructures: Two types of microstructures are to be considered¹⁹; one consisting of discrete droplets, the other of two continuous sponge like interpenetrating phases. It is generally but not unanimously agreed that the discrete droplet phases originate by the classical mechanism of homogeneous nucleation followed by growth, whereas the interpenetrating phases originate by the spinodal decomposition mechanism. The essential difference between the two mechanisms is that spinodal decomposition occurs in the core of the immiscibility gap, where instability is absolute and nucleation is not required. Nucleation is prerequisite in the remainder of the gap, where the system is only metastable. Secondary and higher orders of phase separation can occur, leading to droplets within droplets.

There is evidence⁵⁷⁻⁶¹ that glass microstructure has a dominating influence on the mechanical properties of glass.

T. N. Kesjshyan and M. B. Epelbaum⁶² showed that microhardness was influenced by glass microheterogeneity while in glass-ceramics the microhardness was observed⁶³ to increase with decreasing the grain size of the microcrystals.

The conclusions was observed⁶⁴ on the indentation hardness of a Corning glass (9608). The hardness was assumed to vary in a complex manner with the heat-treatment time which could be correlated to some extent with the observed changes in glass microstructure.

Contribution of the load effect: One of the most

controversial aspect of indentation hardness testing at low loads, is the dependence of hardness on load, which is usually found by considering the relationship between the load (P) and the diameter of diagonal (d) of the impression. In order to discuss this load dependence, several different relationships between load and diagonal have been proposed.

It has been known for some time that the microindentation hardness value increases with decreasing load⁶⁵⁻⁶⁹. This phenomenon appears to be genuine and in no way associated with the instrumental errors or the preparative treatment of the surface.

B. W. Mott⁶⁵ has suggested that the indentation hardness of a given material would be a constant above a critical size of impression but below this size a steady increase in hardness will occur as the load is decreased. Theoretical justification for this has been given on the basis of Orowan's model of work hardening⁷⁰.

H. Buckle⁶⁶ has suggested that it is the presence of covalent regions in the material that is responsible for the observed increase in hardness with decreasing the load.

T. Yoshine⁶⁷ has proposed that the observed load dependence of the microindentation hardness is due to inhomogeneity of the deformation produced by the indenter penetration in material, i.e., the impression are heterogeneous.

N. Gane and J. M. Cox⁶⁸ put forward an alternative explanation suggesting that the increase in hardness at small indentation sizes is due to an increase in the stress necessary to operate dislocation sources. Such a mechanism supposes that the stress required to operate dislocation source is dependent on work-hardening.

M. Braunovic⁶⁹ proposed that the mechanism for load dependence of indentation hardness, is associated with the movement of dislocations introduced by the indenter. The generation of dislocations at a contact interface can be visualised as arising from punching mechanism. This movement may effectively be impeded by the pinning and blocking of these dislocations by

lattice defects such as grain-boundaries, vacancies, solute atoms, precipitates and similar imperfections.

The feature of the elastic recovery of the impression after the indenter is withdrawn from the material is practically negligible in the direction of the diagonal whereas there is a considerable recovery in the direction of depth of the impression^{65,66,71,72}.

Conclusion

Microhardness was found⁷³ to decrease with increasing temperature with two significant irregularities in the neighbourhood of 70° and about 570°. Low frequency internal friction peaks and associated elastic modulus relaxation have been frequently observed in many silicate glasses at about these temperatures. The mechanism causing the peaks is still open to debate⁷⁴. It can be assumed that the microindentations in the cabal glasses investigated might have resulted largely from plastic deformation through co-operative atomic movement depending on the bonding forces between the atoms, ease of mobility of the atomic aggregates and field strength of the respective cations.

The close resemblance in behaviour of the microhardness data and the softening point of the cabal glasses⁵ (Tables I to IV) indicated that the activation energy for the indentation in microhardness phenomenon had some dependence on the softening parameter. A similar conclusion was arrived for metal by H. D. Merchant *et al*⁷⁵.

The high value of diamond pyramid hardness for these cabal glasses can be looked upon through the combined presence of both B_2O_3 and Al_2O_3 in high proportions. The glasses containing B_2O_3 are tough as a result of the disproportionation⁷⁶ of its binding forces into strong forces acting within the molecules and weaker ones acting between adjacent molecules. This distribution of binding forces produces vibrational entropy and opposes propagation of cracks.

The structure of the cabal glasses studied was considered to consist of borate and aluminate

phases⁷⁷⁻⁷⁹. The effect of the introduction of the monovalent alkali ions in replacement of lime could be that alkali ions occupied holes within the interstices formed by BO_3 , BO_4 and AlO_4 groups. The alkali ions resulted in the formation of singly bonded oxygen ions decreasing the coherence of the network. Another suggestion is that the stuffing³⁷ of the network tended to decrease the densification. It can be suggested that some kind of flow was facilitated by the so called 'loose ends' or non-bridging atoms.

Introduction of alkaline earth oxides limited the mobility of non-bridging ions. This was due

to higher field strength and coordination requirement of these ions. The effect of the trivalent or tetravalent metal oxides was attributed to the relatively higher bond strength between the cations and oxygen ions, together with the field strength of the cations.

Summary

Vickers hardness of cabal glasses of base composition CaO 30, B_2O_3 40 and Al_2O_3 30 wt per cent, in which CaO is replaced by Li_2O , Na_2O , K_2O , MgO , ZnO , CdO , SrO , BaO and B_2O_3 by SiO_2 , TiO_2 or ZrO_2 have been studied.

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(Ms received June 5, 1975)

A NOTE ON THE PROPERTIES OF INDIAN MICA IN THIN FILMS

Mica is well known for its excellent dielectric characteristics, particularly low power factor and high dielectric strength. It is used mostly in electrical equipment either as an insulator or as a dielectric for making capacitors.

The suitability of a given piece of mica for a particular end use may be assessed only by determining the properties considered essential for that particular use¹⁻⁴. Unfortunately in the international trade, the quality and the price of mica is decided on the basis of visual appraisal depending on the colour and the type and amount of stains and inclusions. On the basis of such visual examination there are quite a few classes and the price difference is quite substantial from class to class. The selection of a particular class for a specific use is merely on the basis of previous experience that the use of that visual quality mica resulted in a satisfactory product. This type of selection is defective and far from being desirable because there is no scientific evidence contrary to the suitability of the so-called inferior classes of mica for such purpose.

Detailed scientific studies^{3,4} carried out at CGCRI and elsewhere revealed that there is no correlation between the power factor and the physical characteristics like stains, spots and inclusions and as such the method of visual classification has to be supplemented by a method based on actual determination of power factor and other useful electrical characteristics. Apparatus² has also been developed for the rapid classification of mica on the basis of electrical properties.

Properties of mica under normal conditions of temperature and humidity and the effects of thermal ageing and temperature were also studied^{1,2,3} for various classes of visually classified mica. The effects of various types of stains and inclusions were also elaborately studied. Most of these studies were on block samples (7 mils and more in thickness) and on the basis of such studies it is possible to select mica for different engineering services.

The most exacting demands on the quality of mica are, however, made by the mica capacitors of different design for use in radio, radar and other communication equipment requiring high degree of reliability in service under varying conditions of temperature, pressure and humidity. Mica in thin films (1 to 4 mils thick) are required for such uses. Their quality cannot be properly evaluated on the basis of the properties of block mica, because on splitting, the behaviour of mica alters appreciably⁵. It was therefore, considered desirable to study the properties of mica in thin films. Since the actual source of mica plays considerable role in fixing the price of mica, ruby mica from Bihar being sold at a higher price than that from Madras. The present study was undertaken to evaluate film samples of various commercial varieties of mica from different parts of India. Samples collected from Koderma and Giridih in Bihar; Bhilwara and Bhojpura in Rajasthan and Gudur and Nellore in Andhra Pradesh were split into thin films ($1.5 \text{ mil} \pm 0.2 \text{ mil}$ in thickness) and tested for electrical quality, power factor, permittivity, dc resistivity and dielectric strength at room temperature. Properties at elevated temperatures were also studied by measuring dc resistivity and dc electric

*D. Chattopadhyay, S. S. Mandal and S. B. Roy, Central Glass and Ceramic Research Institute, Calcutta-700 032, India

TABLE I

Dielectric properties of Indian mica in thin films (1.5 ± 0.2 mil)

Sl No	Sample Source	Variety	Electrical classification on CGCRI mica test set*	Properties at room temperature (25 ± 2°) relative humidity 51 per cent ± 5 per cent				Properties at 125°			
				Power factor (%)		DC volume resistivity 10 ¹⁴ (Ohm-cm)		Electric strength in oil (kV/mm)		DC volume resistivity 10 ¹⁴ (Ohm-cm)	
				1 mc sec	1 kc sec	Spread	Average	Spread	Average	Spread	Average
1	Bihar	Muscovite Ruby 1st quality	E ₁ —100%	0.022 to 0.041	0.036 to 0.140	0.067 to 0.140	0.12	1.34 to 4.02	2.23	366 to 444	404
2	Madras	-do-	-do-	0.030 to 0.041	0.036 to 0.150	0.079 to 0.150	0.11	1.85 to 6.02	4.64	362 to 538	457
3	Bihar	Ruby stained commercial variety	-do-	0.025 to 0.039	0.033 to 0.160	0.062 to 0.160	0.09	6.62 to 5.88	3.84	264 to 455	353
4A	Madras	Ruby commercial variety	E ₁ —80% E ₂ —20%	0.041 to 0.073	0.048 to 0.10	0.064 to 0.10	0.09	1.76 to 3.71	2.60	283 to 404	350
4B	Madras	Green, commercial variety	E ₁ —55% E ₂ —45%	0.036 to 0.064	0.050 to 0.34	0.077 to 0.34	0.17	1.17 to 1.18	9.03	300 to 404	356
5	Rajasthan	Ruby stained commercial variety	E ₁ —100%	0.036 to 0.040	0.038 to 0.37	0.064 to 0.37	0.14	1.07 to 2.52	1.46	312 to 455	385
6	Bihar	Special slightly greenish in shade	E ₁ —83% E ₂ —17%	0.029 to 0.045	0.037 to 0.51	0.079 to 0.51	0.18	6.82 to 5.03	2.30	330 to 426	391
										4.10 to 10.2	9.19

*pf at 1 mc/s: E₁ < 0.04%; E₂ > 0.04%; E₃ > 0.28%; E₄ > 0.28% < 2.0%

All the samples had electric strength higher than 200 kV/mm

strength at 125°. The results are reported in Table I. The methods of measurement were essentially the same as those reported earlier²⁻⁵.

It is evident from the results (Table I) that

there is hardly any difference between the various commercial varieties of mica films from different parts of the country and all of them are suitable for making mica capacitors.

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CENTRAL GLASS AND CERAMIC RESEARCH INSTITUTE BULLETIN

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High temperature stable ceramic stains: Zirconium-vanadium yellow and green. S. K. Das, M. C. Ghose and S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (3) 63-68 (1977).

The conditions leading to the formation of high temperature stable zirconium-vanadium yellow and green stains and their behaviour in different glaze compositions were studied.

Crystallisation of beta quartz solid solution from $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ glasses. A. K. Chaudhuri, S. K. Das, R. L. Thakur and S. Thiagarajan, *Cent Glass Ceram Res Inst Bull*, **24** (3) 69-75 (1977).

Fine grained glass-ceramics without cracks and very low coefficient of thermal expansion was obtained from $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ glasses.

Photochemical reactions in glasses containing silver. R. N. Dwivedi and P. Nath, *Cent Glass Ceram Res Inst Bull*, **24** (3) 75-80 (1977).

Silver doped photosensitive glasses showed absorption peaks at 315 $m\mu$ and 430 $m\mu$ which were due to atomic

and colloidal silver. Electron microscopic investigation revealed the presence of colloidal silver within the range of 10-20 $m\mu$ and that was responsible for yellow colouration.

Firing characteristics of some clay-grog mixes. S. N. Khosla, R. K. Bedi, C. S. Gupta and S. P. Krishnaswamy, *Cent Glass Ceram Res Inst Bull*, **24** (3) 81-88 (1977).

Firing characteristics of six Jammu clays mixed with 1:1 grog in the range 600°—1100° were determined. Their effect on particle size and pressure resulted in decrease of porosity and increase in shrinkage of the specimens.

Phase composition and reactions of semi-stable dolomite refractories. L. G. Girgis, M. A. Serry and H. K. Embabi, *Cent Glass Ceram Res Inst Bull*, **24** (3) 89-94 (1977).

Suitability for manufacture of semi-stable refractories from a mixture of 90 per cent Egyptian dolomite and 10 per cent talc-magnesite rocks after firing at 1550° for two hours was studied. The actual mineral composition of the raw materials and properties of the end products were determined and the correlation between the determined properties and compositions was also discussed.

CENTRAL GLASS AND CERAMIC RESEARCH INSTITUTE BULLETIN

Vol 24, No 3, 1977

Colorants céramiques stables à haute température: jaune et vert à partir de zirconium-vanadium. S. K. Das, M. C. Ghose et S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (3) 63-68 (1977).

On étudie dans cet article les conditions permettant de produire des colorants jaunes et verts à partir de zircon-vanadium et on examine leurs comportements dans des compositions différentes.

Cristallisation de la solution solide du quartz bêta à partir des verres du système $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$. A. K. Chaudhuri, S. K. Das, R. L. Thakur et S. Thiagarajan, *Cent Glass Ceram Res Inst Bull*, **24** (3) 69-75 (1977).

On a obtenu du verre-céramique sans fissures à grains fins ayant un très faible coefficient de dilatation thermique à partir des verres du système $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$.

Réactions photochimiques dans les verres contenant d'argent. R. N. Dwivedi et P. Nath, *Cent Glass Ceram Res Inst Bull*, **24** (3) 75-80 (1977).

Les verres photosensibles dopés en argent présentent des crochets d'absorption à 315 $m\mu$ et à 430 $m\mu$ ce qui est due à l'argent atomique et colloïdal. L'étude à l'aide de la microscopie électronique met en évidence la présence de particules d'argent colloïdal qui varie de 10 à 20 $m\mu$ ce qui est responsable pour la coloration jaune.

Caractéristiques de cuisson de quelques mélanges chamotte-argile. S. N. Khosla, R. K. Bedi, C. S. Gupta et S. P. Krishnaswamy, *Cent Glass Ceram Res Inst Bull*, **24** (3) 81-88 (1977).

Les auteurs déterminent dans cet article les caractéristiques de cuisson de six argiles provenant de Jammu mélangées avec de la chamotte à un rapport 1 : 1 dans la plage de température de 600° à 1100°. L'influence de dimension de grain et de pression sur les caractéristiques de compacts entraînent un décroissement de la porosité et un accroissement du rétrécissement des échantillons.

Composition de phase et réactions des dolomites réfractaires demistables. L. G. Girgis, M. A. Serry et H. K. Embabi, *Cent Glass Ceram Res Inst Bull*, **24** (3) 89-94 (1977).

L'étude a porté sur l'aptitude d'un mélange de dolomite égyptienne (90%) et de roche talc-magnésite (10%) pour la fabrication des réfractaires demistables en chauffant pendant deux heures à 1550°. On détermine la composition

des minéraux des matières premières et les propriétés des produits finals. On discute ensuite de la relation entre les propriétés déterminées et les compositions.

CENTRAL GLASS AND CERAMIC RESEARCH INSTITUTE BULLETIN

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Hochtemperatur-beständige Keramik-Beizen: Zirkonium-Vanadium gelb und grün. S. K. Das, M. C. Ghose und S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (3) 63-68 (1977).

Die Bedingungen führend zur Entstehung von hochtemperatur-beständigen Zirkonium-Vanadium gelb und grün Keramik-Beizen und ihre Verhalten in den verschiedenen Glasurzusammensetzungen wurden untersucht.

Kristallisation von beta-Quarz-Mischkristalle aus $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ Gläsern. A.K. Chaudhuri S. K. Das, R. L. Thakur und S. Thiagarajan, *Cent Glass Ceram Res Inst Bull*, **24** (3) 69-75 (1977).

Anrissfreie, feinkörnige Glaskeramik mit einem sehr niedrigen Wärmeausdehnungskoeffizient wurde aus $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ Gläsern erhalten.

Photochemische Reaktionen in Silberhaltigen Gläsern. R. N. Dwivedi und P. Nath, *Cent Glass Ceram Res Inst Bull*, **24** (3) 75-80 (1977).

Silber-dotierte lichtempfindliche Gläser ergaben Absorptions-spitzen bei 315 m μ und 430 m μ , die wegen der Anwesenheit von atomischen und kolloidalen Silber verursacht wurden. Elektronenmikroskopische Unter-

suchungen zeigten die Anwesenheit von kolloidalen Silber-Körnchen von 10-20 m μ Grösse, welche für die gelbe Färbung zuständig waren.

Brenneigenschaften von einigen Ton-gemahlene Schamotte Mischungen. S. N. Khosla, R. K. Bedi, C. S. Gupta und S. P. Krishnaswamy, *Cent Glass Ceram Res Inst Bull*, **24** (3) 81-88 (1977).

Brenneigenschaften von sechs Jammu Töne aus Jammu zugemischt mit der 1:1 gemahlene Schamotte im Bereich von 600°-1100° wurden festgestellt. Ihr Einfluss auf Korngrösse und Druck verursachte Porositätsabnahme und Brennschwindungszunahme der Proben.

Phasenzusammensetzungen und Reaktionen der halbbeständigen Dolomit-Feuerfeststoffe. L. G. Girgis, M. A. Serry und H. K. Embabi, *Cent Glass Ceram Res Inst Bull*, **24** (3) 89-94 (1977).

Zweckmässigkeit zur Herstellung der halbbeständigen Feuerfeststoffe aus einer Mischung von 90 prozent Ägyptischen Dolomit und 10 prozent Talk-Magnesit-Felsen wurde nach der Abfeuerung bei 1550° für zwei Stunden untersucht. Die eigentliche Mineralzusammensetzung der Rohstoffe und die Eigenschaften der Endprodukte wurden festgestellt; die Beziehung zwischen der festgestellten Eigenschaften und Zusammensetzungen wurde diskutiert.

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HIGH TEMPERATURE STABLE CERAMIC STAINS : ZIRCONIUM-VANADIUM YELLOW AND GREEN

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Introduction

Zirconium stains have gained wide acceptance in ceramic industry, particularly in sanitarywares and wall tiles. These stains are stable at high temperature firing conditions and have improved shades of colour. At present, zirconium stains of yellow, blue and green colours are produced commercially in some of the technologically advanced countries. The demand for these colours in India is mostly met from imports.

With a view to achieving self-reliance, the work for developing high temperature stable ceramic stains from indigenously available zirconia was taken up at the Institute. The detailed investigations in the preparation of zircon-vanadium blue and zircon-praseodymium yellow stains were reported earlier¹.

This paper presents studies in the preparation of zirconium-vanadium yellow and green stains for use in different high temperature glazes commonly used in pottery industry.

Literature on the mechanism of colour formation

Basically, zirconium stains may be divided into two classes: (i) those in which sufficient silica is present which results in the formation of zircon during calcination; and (ii) those in which no silica is present and thus zirconia remains unchanged after calcination.

Zircon-vanadium blue and zircon-praseodymium yellow stains contain equimolar quantities of ZrO_2 and SiO_2 in which zirconia and silica

react to form zircon. Tetravalent colouring ions like V^{4+} or Pr^{4+} enter the zircon lattice during calcination¹⁻⁴.

Zirconium-vanadium yellow: These stains do not contain silica in the composition and the mechanism of their formation is quite different from that of Zr-V blue and Zr-Pr yellow stains. X-ray diffraction analysis shows that zirconia in the Zr-V yellow stain remains unchanged after calcination and the formation of yellow colour of the stain has been attributed to the presence of a colloidal film of V_2O_5 being deposited or adsorbed on the surface of zirconia particles². Considering the stability of the stain against molten glaze components, an alternative explanation for the formation of Zr-V yellow stain has also been suggested⁵. Fine crystals of ZrO_2 are formed from the decomposition of zirconium-pyrovandate (ZrV_2O_7). Vanadium pentoxide then gets drawn into the interspaces of the crystal aggregates of ZrO_2 , which are formed on further heating to higher temperatures. This is believed to be the reason why higher calcination temperatures (1250° and above) are required for producing Zr-V yellow stain of high intensity. The crystal aggregates of ZrO_2 thus give better protection to the absorbed V_2O_5 against the glaze and the stain becomes more stable. The answer for the formation of Zr-V yellow stain may well be a combination of the above two possible explanations.

Zirconium-vanadium green: X-ray studies² as well as the microscopic studies⁶ of Zr-V green stain have established the presence of a mixture of zircon and zirconia and aggregates of blue and

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yellow coloured crystals. Also, the green stain is stated to contain vanadium in pentavalent and in tetravalent forms and it is a mixture of zircon-vanadium blue and zirconium-vanadium yellow stains².

Sodium fluoride which acts as an essential mineraliser in the formation of zircon in the Zr-V blue stain is not required in the preparation of the Zr-V green stain. V. I. Matkovich and P.M. Corbett⁷ have shown that the formation of zircon from zirconia and silica can also occur in the presence of V_2O_5 only.

Experimental

Raw materials: Ammonium metavanadate (98 per cent NH_4VO_3), quartz powder (99 per cent SiO_2) and indigenously available zirconia (99.5 per cent ZrO_2) and yttrium oxide (99 per cent Y_2O_3) were used.

Preparation of the stain: The mixing of the stain batch was made by wet grinding in porcelain milling jars. The batch was then calcined in refractory crucibles, in electrically heated muffle furnace with optimum time temperature schedule. After calcination, the stain was sieved through 100 mesh BS sieve and then thoroughly washed with hot water to remove unreacted vanadium pentoxide. The stain was then dried and finally sieved before storing.

Glazes: Three types of fritted borosilicate glazes (lead-free transparent, lead-free zircon opacified and lead-bearing zircon opacified) which are commonly used in sanitaryware and pottery industries, were used in evaluating the intensity and colouring shades obtained from the stains. The glaze compositions are shown in Table I. The stains were wet milled with the glaze together with clay (10 per cent) and zircon opacifier (2 to 3 per cent) as mill additions. The glaze coated tiles were fired in electrically heated muffle furnace over a three-hour cycle with soaking for one hour at glost firing temperature of 1050-1100°.

Results and discussion

Zirconium-vanadium yellow: These stains were

TABLE I
Molecular formulae of the fritted glazes

Constituents	Glaze G-1 (lead-free transparent)	Glaze G-2 (lead-free opaque)	Glaze G-3 (lead-bearing opaque)
SiO_2	3.50	3.48	3.13
ZrO_2	—	0.14	0.26
Al_2O_3	0.35	0.35	0.37
B_2O_3	0.60	0.60	0.38
PbO	—	—	0.02
ZnO	0.30	0.30	0.25
BaO	—	—	0.06
CaO	0.40	0.40	0.23
MgO	—	—	0.17
KNaO	0.30	0.30	0.27
Glost firing at (°C)	1050-1100	1050-1100	1050-1100

prepared by blending and calcining a mixture of zirconia (ZrO_2) and ammonium metavanadate (NH_4VO_3) to temperatures of 1250-1280° in an oxidising atmosphere. The compositions of Zr-V yellow stains are shown in Table II. In the formation of yellow stain, the calcination schedule was required to be controlled within critical limits. The colour of the stain was observed to increase with increased calcination temperatures and reached a maximum at about 1280°. Rapid calcination schedule reduced the colour intensity of the stains. Recalcination at 1280° or calcination at temperatures above 1280° did not show any noticeable improvement in the intensity of the stain. The calcined stain had colours varying from Khaki-yellow to brownish-yellow, which after repeated washing for 3 to 4 times with hot water yielded mustard-yellow colour of the stain. The intensity and colouring effects of various compositions of the stains were evaluated by their application in the lead-free opaque glaze (G-2, Table I). In the preparation of the Zr-V yellow stain, it was found to be essential to wash the calcined stain thoroughly to remove unreacted vanadium pentoxide which

otherwise resulted in the formation of a dirty yellow shade or might combine with the calcium in the glazes forming calcium vanadate causing dimples in the fired glaze⁸.

Table II shows that the colour intensity of the stains 1, 2 and 3 increased with increasing amounts of the vanadate in the batch and yielded maximum intensity in stain 3 when the amount of the ammonium vanadate corresponded to 5 per cent. The intensity remained unchanged, as in the stain 4, with further increase of ammonium vanadate (10 per cent). This indicated that a limited quantity of vanadium pentoxide was responsible in the formation of yellow colour, thus limiting the intensity of the stain.

Vanadium pentoxide (V_2O_5) can also be used in place of ammonium metavanadate but the latter being water soluble, was found preferable to use as it effected better dispersion in the batch mixture. The colour of stain 5 prepared with the use of V_2O_5 (5 per cent) was brownish-yellow which required considerable washing for obtaining a good yellow shade in the fired glaze.

The addition of potassium nitrate (4 per cent) as an oxidising agent in the batch composition

(stain 6) did not produce any advantageous effect on the colour intensity of the stain.

An attempt to produce the yellow stain by replacing zirconia with the cheaper zircon sand as in the stain 7 only produced a blackish-brown colour resulting in a very dirty and lighter yellow shade in the fired glaze.

The addition of a small amount of titanium dioxide (TiO_2) to the basic composition of Zr-V yellow stain was found to shift the yellow colour more towards creamish side. The stain 8 containing TiO_2 (1.5 per cent) produced an intense yellow colour of the stain but the colour tone in the fired glaze shifted to creamish yellow side. Increase of the content of TiO_2 (4 per cent) as in the stain 9, either with or without the use of a trace of boric acid (0.5 per cent), reduced the colour intensity of the stains and produced a lighter creamish-yellow shade in the fired glaze.

The addition of a small amount of yttrium oxide (Y_2O_3) to the basic composition of Zr-V yellow stain was found to produce orangish-yellow shade in the fired glaze. The orangish effect was maximum with the use of Y_2O_3 (2 per cent) as in the stain 10. Further increase of

TABLE II

Zirconium-vanadium yellow stains

Constituents	Stain numbers											
	1	2	3	4	5	6	7	8	9	10	11	12
ZrO_2	97	96	95	90	95	90		93.5	90	93	90	80
NH_4VO_3	3	4	5	10	—	6	10	5	6	5	5	5
V_2O_5					5							
$ZrSiO_4$							90					
KNO_3						4						
TiO_2								1.5	4			10
Y_2O_3										2	5	5
Colouring shade	LY	Y	IY	IY	Y	Y	DY	ICY	LCY	YO	YO	LY

LY-light yellow; Y-yellow; IY-intense yellow; DY-dirty yellow; ICY-intense creamish yellow; LCY-light creamish yellow; YO-yellowish orange

Y_2O_3 (5 per cent) did not produce any increase in the orange shade (stain 11). Effect of TiO_2 (10 per cent) along with Y_2O_3 (5 per cent) produced a lighter yellow shade without any orange tinge in the fired glaze (stain 12).

The fired glaze finish obtained from Zr-V yellow stain had a creamish-yellow colour as against a lemon-yellow colour obtained from Zr-Pr yellow stain^{1,2}. The Zr-V yellow stain could be used both in the lead-bearing (G-3) as well as in lead-free glaze (G-2) compositions with no significant change in the colouring shade. The Zr-V yellow stains were tried in the glazes as shown in Table I. It was observed that the two glazes (G-2 and G-3) with 2 to 3 per cent zircon as mill added opacifier produced maximum uniformity and intensity in colouring shade. The lead-bearing glaze (G-3), however, showed a marginally lower colour intensity than that obtained from the lead-free (G-2) glaze. In the case of the transparent glaze (G-1) without zircon opacifier, a comparable colouring shade could be obtained only with high content (10 per cent) of the stain. The colouring effect obtained in G-1 with the use of 2 to 5 per cent of the stain was lacking in opacity and uniformity.

About 1 to 7 per cent of the Zr-V yellow stain could be used in the glazes G-2 and G-3. Less than this produced an ivory shade and more than this did not improve the colour intensity. An intense yellow colour was obtained with the

use of 5 per cent of the stain, the intensity being only marginally increased up to 7 per cent. Overgrinding of the glaze also resulted in weakening the colour intensity.

The colouring effect of Zr-V-Y stain was more intense than that of Zr-V yellow and had a more reddish characteristic. A good orange-yellow colour was obtained with the use of 10 per cent of the stain 10 (Table II) in the transparent glaze (G-1) but the orange tone in the colouring shade was reduced when the stain was used in the glazes (G-2 and G-3) either with or without the use of 2 to 3 per cent zircon as mill added opacifier.

The Zr-V stains showed intense colour with firing of the glazes at 1050 to 1100° and only a marginal fading of colour was observed with increased firing temperatures up to 1300°. Such fading of colour could be minimised by increasing the content of the stain by 1 to 2 per cent. The stains (5 per cent) also produced good yellow colour in transparent enamels for sheet iron with firing temperatures of 800 to 820°.

Zirconium-vanadium green: These stains were prepared by calcining a mixture of zirconia (ZrO_2) and ammonium metavanadate (NH_4VO_3) with a limited quantity of silica (SiO_2) at temperatures of about 1200° in an oxidising atmosphere. The compositions of the Zr-V green stains which were studied during this investigation are shown in Table III. The stains had a greenish-khaki colour and the intensity and the

TABLE III

Zirconium-vanadium green stains

Constituents	Stain numbers									
	21	22	23	24	25	26	27	28	29	30
ZrO_2	72	74	80	70	66	72	72	72	72	70
SiO_2	18	16	10	20	24	18	18	18	18	18.5
NH_4VO_3	10	10	10	10	10	5	7.5	12.5	15	10
TiO_2	—	—	—	—	—	—	—	—	—	1.5
Colouring shade	G	YG	YG	BG	BG	YG	YG	BG	BG	G

G-green; YG-yellowish green; BG-bluish green

colouring effects were evaluated by their applications in the lead-free opaque glaze (G-2, Table I).

In addition to the chemical composition, the shade of the colour of the Zr-V green stains was observed to depend largely on the calcination temperatures. Recalcination at 1200° or above resulted in the formation of yellowish-green colour, while lowering the calcination temperatures to about 1050° resulted in the formation of a bluish-green colour. In the preparation of the Zr-V green stain, it was found essential to wash 3 to 4 times the calcined stain with hot water to remove unreacted V_2O_5 which otherwise caused a dirty-yellowish tinge in the colouring shade.

The proportions of ZrO_2 and SiO_2 in the composition (Table III) of the Zr-V green stain had a very important bearing on its colouring shade. When the molar proportions of ZrO_2 : SiO_2 were in the range of 2:1 (stain 21), a green shade was obtained. The stains 22 and 23 containing lower proportion of SiO_2 produced a yellowish tinge in the green shade and the yellowish characteristic was increased with further decrease of SiO_2 content. The stains 24 and 25 containing higher proportion of SiO_2 produced a bluish tinge in the green shade and the bluish tinge increased with further increase of the proportion of SiO_2 .

The fineness of ZrO_2 and SiO_2 used in the preparation of Zr-V green stains was —300 mesh and —200 mesh BS sieve respectively. Increase in the fineness of quartz powder or use of silica sol in its place in the composition (stain 21), did not show any advantageous effect on the colour intensity of the stain.

The shade of the Zr-V green stain was also observed to vary with the content of ammonium metavanadate in the composition. The stains 26 and 27 containing lower amounts of the vanadate (5 and 7.5 per cent approximately) produced a greenish-yellow shade. The yellow tinge in the greenish shade was also observed to decrease with increasing content of the vanadate and a good green shade was obtained with NH_4VO_3 (10 per cent) as in the stain 21. Further increase

of the vanadate, however, produced bluish green shades (stains 28 and 29).

The addition of sodium fluoride as a mineraliser in the formation of Zr-V green stain was found to have no advantageous effect. The stain 21 which produced a good green shade, showed a slight decrease in colour intensity with the addition of sodium fluoride (3.5 parts) in the batch.

The addition of a small amount of TiO_2 (1.5 per cent) in the composition of the green stain 30 was found to have an advantageous effect of producing a green shade of pleasing softness. But further increase of the content of TiO_2 (3 per cent) changed the shade to yellowish green.

The Zr-V green stains are extensively used for producing pastel shades. The glaze formulae used with the stains are not critical, as with the chromium and other green colourants^{5,9}. Like other zirconium stains, Zr-V green is normally used with 2 to 3 per cent zircon as mill added opacifier to obtain a satisfactory stabilising effect. The Zr-V green stains were tried in the glazes as shown in Table I. It was observed that the lead-bearing opaque glaze (G-3) produced a bluish tone in the green shade, whilst the lead-free opaque glaze (G-2) produced a yellowish tone in the green shade. A good green colour was also obtained in the transparent glaze when a high content of the stain (10 per cent) was used without any mill added zircon opacifier.

Zr-V green stain could be used in the glazes over a range of about 5 to 10 per cent. Below 5 per cent a pale greenish colour was obtained and light to medium green shades were produced by the addition of 5 to 7 per cent of the stain. The intensity only marginally increased with 10 per cent of the stain and more than 10 per cent had no advantageous effect. Over-grinding of the glaze resulted in weakening the colour intensity.

The stability of the Zr-V green stain at high temperature firing conditions was observed to be similar to that of Zr-V yellow stain.

A wide range of bluish-green and yellowish-green shades was obtained by blending Zr-V

blue stain with either Zr-V or Zr-Pr yellow stains in varying proportions. A very pleasing bluish-green shade was obtained, *eg.* by mixing two parts by weight of Zr-V blue with one part of Zr-Pr yellow. Blending of two parts by weight of Zr-V blue with one part of Zr-V yellow also produced a nice yellowish-green colour. These three types of zirconium based blue and yellow stains were thus found to be quite compatible with each other for obtaining suitably blended colours.

Summary

The intensity of the Zr-V yellow stain reached a maximum with a calcination temperature of 1280° but the colour intensity was reduced if the calcination schedule was too rapid.

The intensity of the Zr-V yellow stain reached a maximum with ammonium vanadate of 5 per cent. Further increase of the vanadate did not improve the intensity.

The Zr-V yellow stain could not be prepared by replacing ZrO_2 with zirconium silicate ($ZrSiO_4$).

Addition of an optimum amount of 2 per cent yttrium oxide to the basic composition of the Zr-V yellow, produced an orangish-yellow shade and further increase of the Y_2O_3 did not in-

crease the orange tone any further.

Calcination temperatures of the Zr-V green stain effected the final colour. Calcination temperatures above 1200° resulted in the formation of yellowish-green colour. Calcination below 1200° produced a bluish-green colour.

The colouring effect and intensity of the Zr-V green stain largely depended on the proportions of ZrO_2 and SiO_2 . A good green colour was obtained with molar proportion of ZrO_2 and SiO_2 in the range of 2:1.

The colouring effect and intensity of the Zr-V green stain depended on the content of ammonium metavanadate. The colour intensity was maximum with 10 per cent of the vanadate.

The Zr-V yellow and green stains worked best in zircon opacified glazes and the addition of 2 to 3 per cent of zircon opacifier with the stain was preferable to stabilise the colouring shade.

The colouring effect and intensity of both the yellow and green stains were limited and there was no noticeable improvement with the stains above 10 per cent.

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CRYSTALLISATION OF BETA QUARTZ SOLID SOLUTION FROM $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ GLASSES

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Introduction

High quartz solid solutions appear metastably as the first crystallisation products from diverse glass compositions¹⁻⁴. The transformations leading to the precipitations of the β -quartz solid solutions as well as the subsequent transformations of the β -quartz solid solutions to other crystals are accompanied by considerable volume changes. Dilatometry is, therefore, a very useful technique for studying these transformations. The resulting crystallisation products in these systems have a range of coefficient of thermal expansion from negative through zero to positive values⁵. The sequence and rate of transformations have a profound influence on coefficient of thermal expansion as well as on the microstructure of the final products. Dilatometry, differential thermal analysis, X-ray and microscopic methods were used to study the course of transformation of lithia-alumina-silicate glasses.

Experimental

The glass compositions as calculated from the batch are given in Table I. Laboratory reagent chemicals were used to make the batches except for compositions C and D where lepidolite was used for part of the batches. The glass meltings were carried out in batches of 3 kg each in electrical or oil fired furnace in oxidising atmosphere. The melting temperature ranged from 1450° to 1600°. The glass was pressed cast in the form of rectangular rods of about 150 × 6 × 6 mm and annealed. Part of the glass was poured in the form of thin rods of about 2 to 3 mm dia and

allowed to cool in air. This was used for differential thermal analysis.

The dta was performed on glass powders (−200 mesh +400 mesh ASTM) placed in platinum beakers against α -alumina as the reference material in Netzsch thermal analyser 404. The heating rate was 10° per minute. The curves *i* in Figs 1 to 4 are the dta curves.

Bar samples of 50 × 5 × 5 mm was used for recording the linear thermal expansion in a Netzsch dilatometer. The heating rate was 5° per minute. The curves *ii* in Figs 1 to 4 are the dilation curves. The mean coefficient of thermal expansion from 30° to 300° was separately determined for the glasses after heat-treatment up to the predetermined temperatures (700°, 800°, 900°, 1000° and 1100°) and then cooling to room temperature naturally in air. These coefficients are plotted as a function of the heat-treatment temperatures in curves *iv* (Figs 1 to 4). The density of the glasses with the same heat-treatment as above was determined at room temperature from the loss of weight in water. The density values are plotted in curves *iii* (Figs 1 to 4).

The microstructure of the glasses with different heat-treatments was studied in a Hitachi transmission electron microscope HU 11E. A two stage replica method was used. The electron micrographs are presented in Figs 5 to 8. The crystal phases were identified by X-ray diffraction.

Discussion

In β -quartz solid solutions, the existence of holes or channels in the structure makes possible

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the stuffing of the structure⁶ with cations like Li^+ , Mg^{2+} , Zn^{2+} and Fe^{2+} . The β -quartz without these stuffings is highly unstable at the room temperatures and reverts easily to the stable α -form. The stuffing makes the structure highly metastable so that the β -quartz persists

indefinitely at the room temperature. The formation of the stuffed β -quartz is accompanied by a volume decrease. Besides the hole or channel stuffing other mechanisms have also been suggested in the literature for the accommodation of these cations^{4,7,10}. This involves the substitution

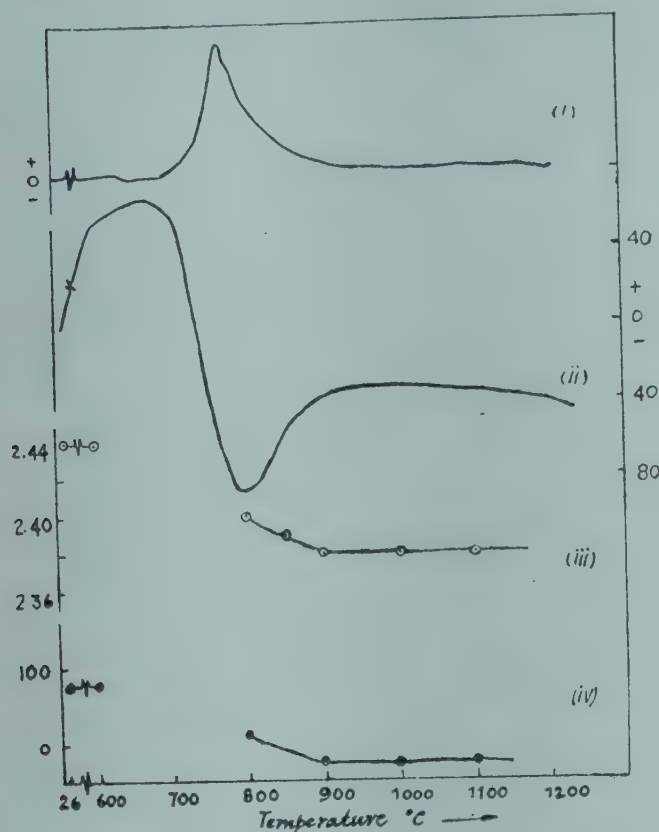


Fig 1

Properties of glass A: temperature vs emf (curve i); temperature vs dilatation, μ/mm (curve ii); temperature vs density, gm/cc (curve iii) and temperature vs coefficient of thermal expansion, $\alpha \times 10^7$ from room temperature to 300°C (curve iv)

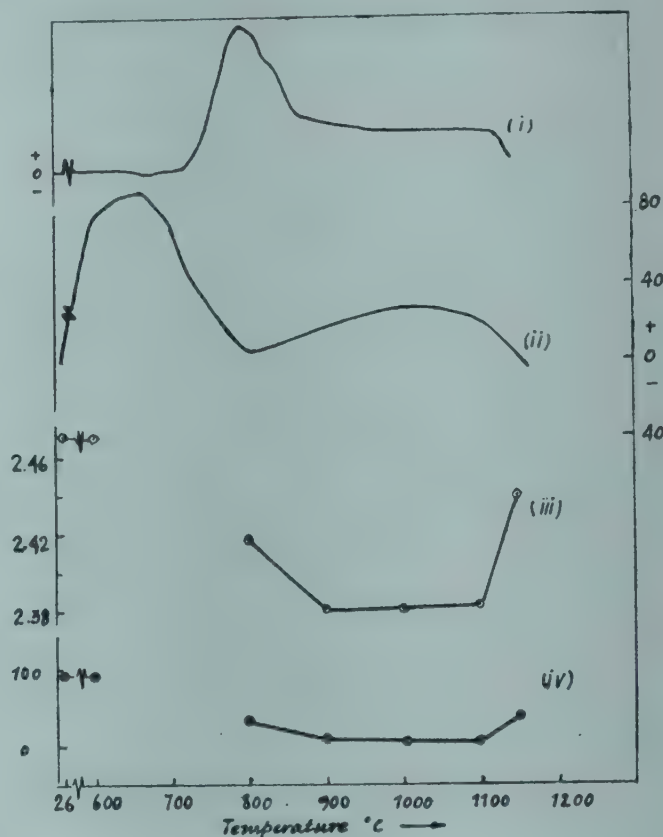


Fig 2

Properties of glass B: temperature vs emf (curve i); temperature vs dilatation, μ/mm (curve ii); temperature vs density, gm/cc (curve iii) and temperature vs coefficient of thermal expansion, $\alpha \times 10^7$ from room temperature to 300°C (curve iv)

TABLE I

Glass composition calculated from the batch (wt per cent)

Glasses	SiO_2	Al_2O_3	Li_2O	ZnO	P_2O_5	MgO	R_2O^*	Fe_2O_3	CaO	B_2O_3	Overall additions gm/100 gm of glass				
											TiO_2	ZrO_2	CaO	F	As_2O_3
A	54.0	33.0	10.0	—	—	—	—	—	—	3.0	2.0	0.5	—	—	—
B	54.0	33.0	10.0	—	—	—	—	—	—	3.0	2.0	0.5	2.0	—	—
C	61.8	25.0	4.6	—	—	3.5	4.2	0.9	—	—	0.85	0.64	—	0.3	0.2
D	55.6	24.4	3.5	1.8	12.8	0.9	0.5	0.3	0.4	—	2.0	1.8	—	—	0.3

*alkalies other than Li_2O

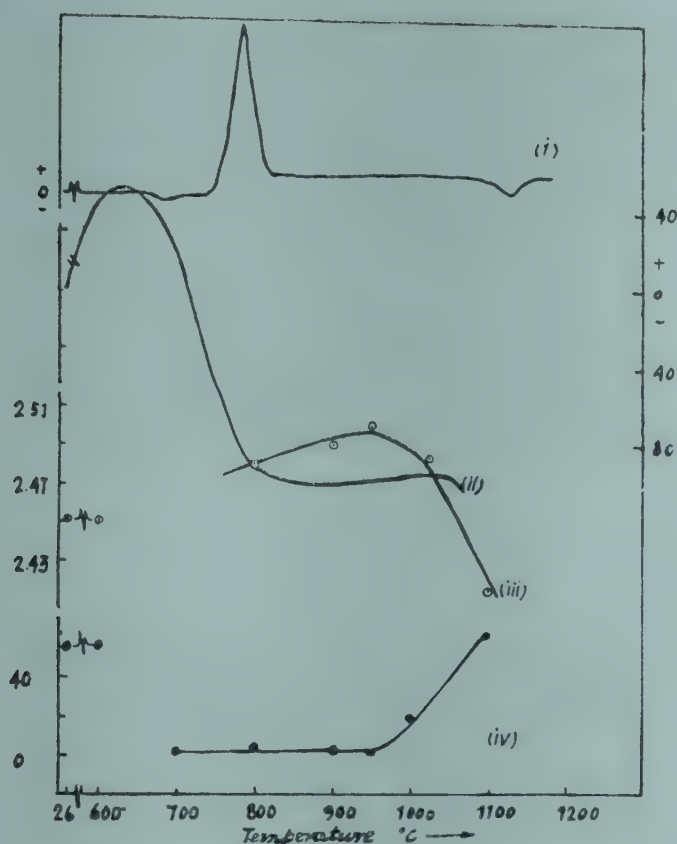


Fig 3

Properties of glass C: temperature *vs* emf (curve *i*); temperature *vs* dilatation, μ/mm (curve *ii*); temperature *vs* density, gm/cc (curve *iii*) and temperature *vs* coefficient of thermal expansion, $\alpha \times 10^7$ from room temperature to 300°C (curve *iv*)

of the tetrahedrally coordinated framework Si^{4+} by other cations with network forming capability such as Al^{3+} and Ti^{4+} . J. Petzoldt⁴ suggested a complex substitution of the network former such as Al^{3+} plus P^{5+} replacing 2Si^{4+} . A. S. Perrotta¹¹ suggested Al^{3+} plus As^{5+} replacing 2Si^{4+} .

The mineralogical composition of the crystallisation of β -quartz solid solution products from lithia-alumina-silicate glasses ranges from β -eucryptite ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) on the low silica side to spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) on the high silica side. The heat-treatment at higher temperatures of β -quartz is likely to yield break down products due to the exsolution of the stuffed or substituted cations. The break up process is accompanied by a volume increase.

The growth morphology and grain size of the β -quartz solid solution from the glasses greatly

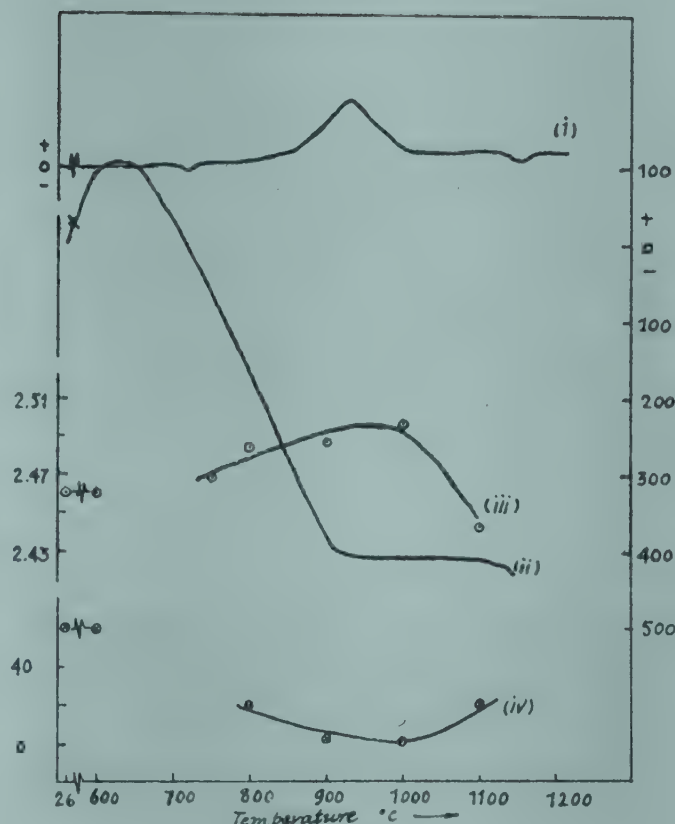


Fig 4

Properties of glass D: temperature *vs* emf (curve *i*); temperature *vs* dilatation, μ/mm (curve *ii*); temperature *vs* density, gm/cc (curve *iii*) and temperature *vs* coefficient of thermal expansion, $\alpha \times 10^7$ from room temperature to 300°C (curve *iv*)

influenced the gross thermal expansion behaviour. With coarse grains the final material developed numerous cracks. A properly nucleated and fine grained crystallisation was essential to obtain reasonably crack-free glass-ceramic in this system. The resultant thermal expansion behaviour of the crack-free glass-ceramic was decided by the relative compositional magnitudes of the β -quartz solid solution and the residual glass and crystal phases.

The compositions A and B: The compositions A and B were close to eucryptite with 0.125 mole of Al_2O_3 substituted by B_2O_3 . The composition B in addition contained an overall addition of 2 per cent CaO .

The dta (curve *i*) of glasses A (Fig 1) and B (Fig 2) showed first an endotherm due to the glass transformation followed by an exotherm corresponding to the primary crystallisation of

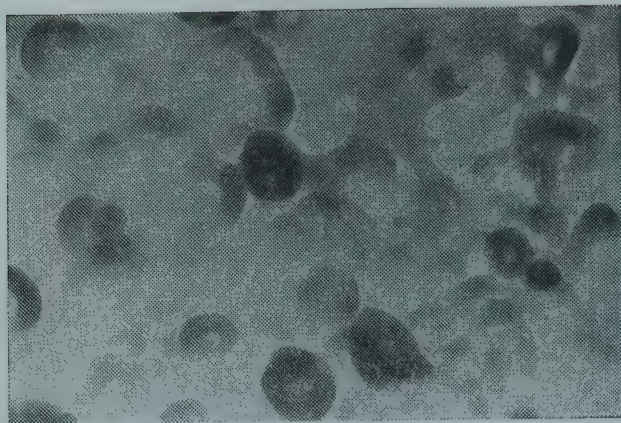


Fig 5i

Electron micrograph of glass A heated to 800° ($\times 62000$)



Fig 5ii

Electron micrograph of glass A heated to 1000° ($\times 40000$)



Fig 6i

Electron micrograph of glass B heated to 800° ($\times 8300$)

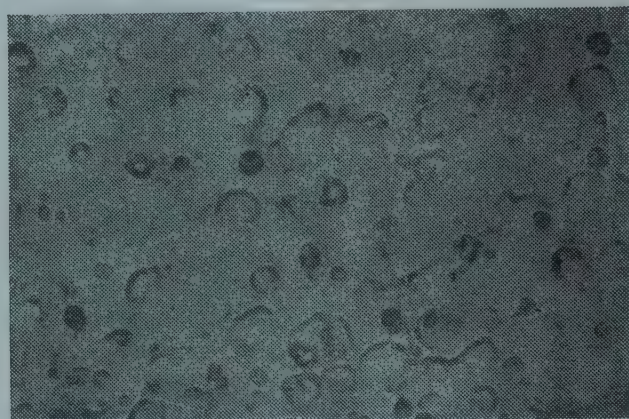


Fig 6ii

Electron micrograph of glass B heated to 1000° ($\times 20000$)

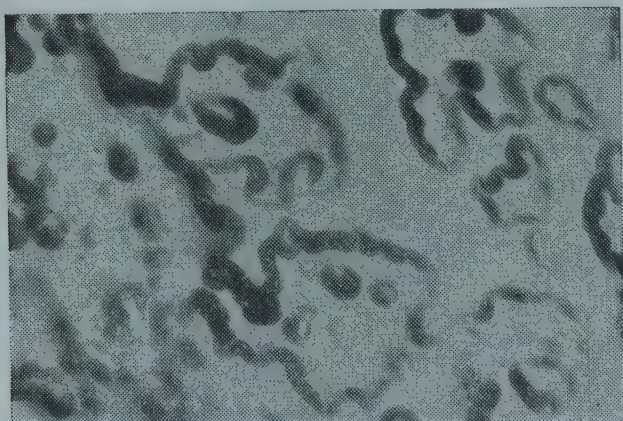


Fig 7i

Electron micrograph of glass C heated to 800° ($\times 24000$)

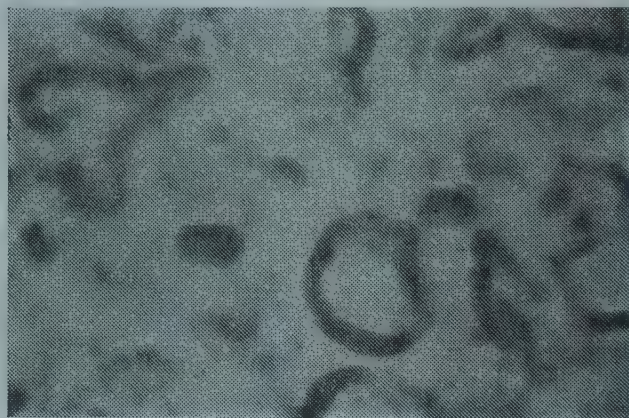


Fig 7ii

Electron micrograph of glass C heated to 1000° ($\times 30000$)

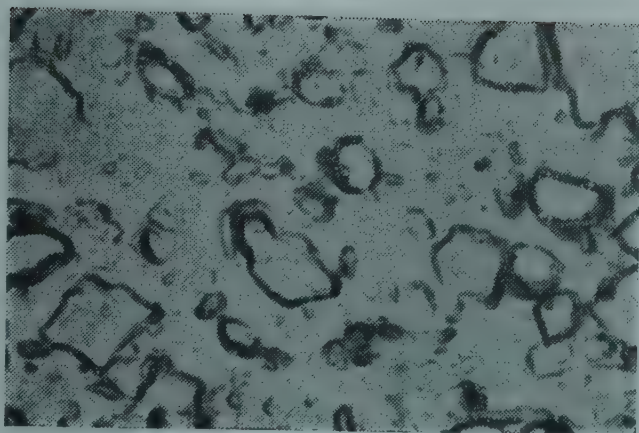


Fig 7iii

Electron micrograph of glass C heated to 1100° ($\times 12000$)

β -eucryptite. The exotherm rose sharply and slowed down after crossing the peak.

The dilatation (curve *ii*, Fig 1) of glass A first showed a sharp glass transformation (mt pt) followed by a steep fall arising from viscous flow. The viscous flow was arrested by the onset of crystallisation of the primary phase. The progress of crystallisation was very fast. The subsequent positive slope in the dilatation curve *ii* (Fig 1) corresponded to the appearance of lithium metasilicate. Above 1000° lithium spinel and spodumene also were detected by X-ray diffraction. These were reflected in positive increase in the dilatation rate. The sharp dip at the high temperature end of the curve indicated the onset of melting.

The density curve *iii* (Fig 1) also followed a similar trend.

The coefficient of thermal expansion of glass A as function of the temperature at which the glass was heat-treated (curve *iv*, Fig 1) decreased from a near zero value at 800° to negative constant value at 900° and above.

The dta (curve *i*) of glass B (Fig 2) showed a broadened exotherm compared to glass A (curve *i*, Fig 1). The peak was shifted to a higher temperature. The addition of CaO increased the viscosity of the glass in the range of temperature for the crystallisation thereby increasing the kinetic barrier for the process of crystallisation. This slowed down the rate of

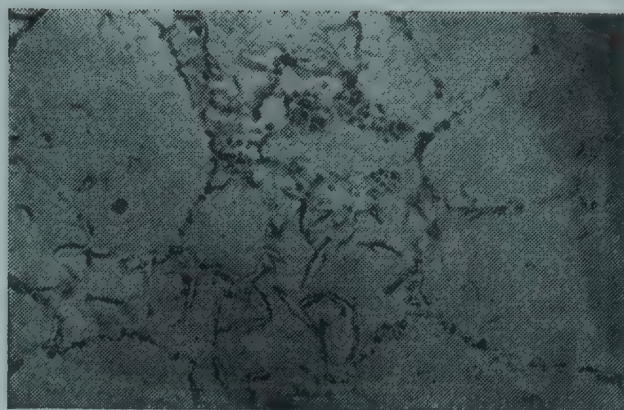


Fig 8i

Electron micrograph of glass D heated to 800° ($\times 10000$)

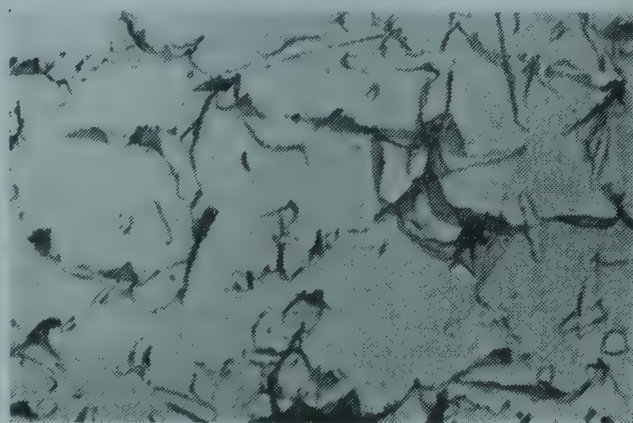


Fig 8ii

Electron micrograph of glass D heated to 1100° ($\times 9200$)

growth of the β -quartz. It pushed up the temperature range for the exsolution and dissociation of the products to much higher values as reflected in the dilation curve *ii* of Fig 2. Probably the crystallisation of some residual glass at temperatures above 1000° leads to further densification (curve *iii*, Fig 2).

The samples of glasses A and B heat-treated at 750° and cooled to room temperature showed extensive cracks. The samples heated at 800° and above did not reveal visible cracks.

The electron micrographs of the glasses A and B heat-treated at different temperatures are given in Figs 5 and 6. The micrographs of glass B heated at 800° (Figs 6i and 6ii) showed large phase separated regions. T. I. Barry *et al*¹² observed similar features and identified them as

domains comprising polytwinned crystals with very low crystallinity. They found that the crystal faces are blurred when the specimens were etched with HF of concentration 1 per cent or more.

The glasses C and D (Table I) contained higher amount of SiO_2 and lower amount of Al_2O_3 and alkalis than glasses A and B. The composition C contained 3.5 per cent of MgO and 0.3 per cent of F. The composition D contained very little MgO , 12.8 per cent of P_2O_5 but no F. Small amounts of ZnO , Fe_2O_3 and CaO were also found to be present in D.

The glass C started crystallising at 730° . The dta exotherm (curve *i*, Fig 3) was quite sharp and the crystallisation was completed around 820° . The dilation curve *ii* (Fig 3) flattened around 820° . With further heating the exolution of the β -quartz took place giving rise to the break down products and volume increase. Magnesia-alumina spinel and mullite are detected by X-ray diffraction in glasses heat-treated between 900° and 1000° . The coefficient of thermal expansion (curve *iv*, Fig 3) increased in this temperature range. The coefficient of expansion remained close to zero for the samples heat-treated between 700° and 950° . The precipitation of β -quartz at fairly low temperature was possible because of fluorine in the batch. Fluorine lowered the viscosity and the kinetic barrier for crystallisation¹³. Higher diffraction lines characteristic of layer lattice were observed in the crystallised samples of glass C around 10\AA .

The glass D had a higher crystallisation temperature than the other glasses. The dta curve *i* (Fig 4) was broader and the peak was shifted to higher temperature around 920° . Similar trend was noticed in the

dilatation curve *ii* of Fig 4 which flattened out after 900° . This showed that the β -quartz was stable against exsolution and dissociation in the glass. The presence of P_2O_5 probably helped in slowing down the growth rate of the β -quartz crystals and in raising the transformation temperature as also in preventing the dissociation products up to 1000° . The coefficient of thermal expansion (curve *iv*, Fig 4) reached a value close to zero after heat-treatment at temperatures between 900° and 1000° .

The electron micrographs of the glasses C and D with different heat-treatments are given in Figs 7 and 8. The domains of polytwinned crystals of low crystallinity referred to by T. I. Barry *et al*¹² can be observed in Fig 8i.

Summary

Crystallisation of β -quartz solid solutions from lithia-alumina-silicate glass systems containing additions of B_2O_3 , P_2O_5 and others were studied: (i) The sequence of crystallisation of β -quartz solid solution and their subsequent break down can be followed by dilatometry and dta; (ii) The growth rate of β -quartz solid solution has to be carefully controlled (such as by the addition of CaO , P_2O_5 and of mixed alkalis) to obtain a fine grained glass-ceramics without cracks and with very low thermal expansion coefficients. The addition of MgO , ZnO , P_2O_5 , As_2O_3 gave rise to the stuffed derivatives of β -quartz that were stable up to a fairly higher temperatures.

Acknowledgment

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PHOTOCHEMICAL REACTIONS IN GLASSES CONTAINING SILVER

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Introduction

When silver compounds are introduced in glass, they behave like alkali compounds as long as the relative amount of silver is below 0.5 per cent¹. Elemental silver is not very soluble in glass. Metallic silver will, therefore, be precipitated under certain conditions of temperature and glass composition. When the glass is reheated, the metal atoms aggregate to form particles of colloidal size. The glass becomes yellow and the fluorescence is shifted to longer wavelengths with decrease in its intensity. Further growth of the

particles changes the colour from yellow to brown and finally to grey². Nucleation is enhanced by irradiation and silver atoms are precipitated at lower temperature³.

B. Bogitch⁴ found that sodium silicate glasses containing more than 1 per cent of silver oxide began to darken when exposed to day light over a period of 2-3 months.

Photosensitive glasses containing silver were first proposed by W. H. Armistead⁵. When glass doped with silver and cerium is exposed to uv radiation, the silver ion accepts an electron from the Ce^{3+} ion and changes into atomic silver. On heat-treatment the silver atoms coagulate and form colloidal silver particles.

S. D. Stookey⁶ developed a photosensitive glass from $SiO_2-Li_2O-K_2O-Al_2O_3$. K. Barth⁷ observed that the intensity of colour increased

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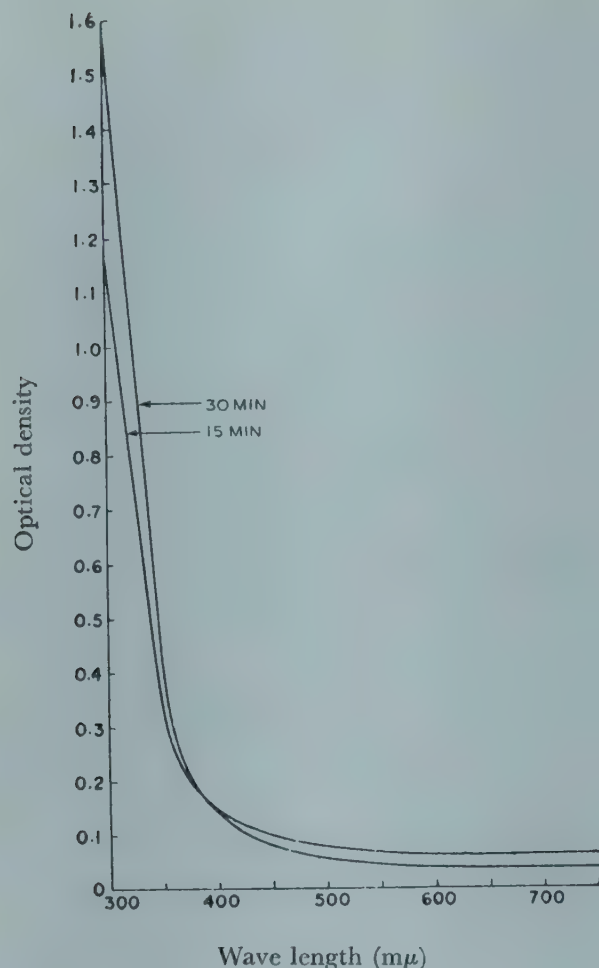


Fig 1

Effect of duration of exposure on colour. Glass exposed but not developed

with longer exposures, longer development periods and higher development temperatures. Heating the glass during ultraviolet exposure remarkably increased the photosensitivity, and above 300° development was accomplished simultaneously with exposure⁸. EPR spectra⁹ of photosensitive silver glass irradiated by X-ray revealed the formation of silver atoms by entrapment of electrons by Ag^+ and Ag^{2+} ions. Similar observations were made by R. Yokota¹⁰. A. A. Gorbachev, Y. M. Polukhin, A.M. Ravich and L. M. Yusim¹¹ observed that irradiation resulted in the appearance of an absorption line in the 275 mμ region and the intensity of this line decreased with increasing temperature. The decrease was accompanied by the appearance of a new line at 405 mμ. M. Tashiro and N. Soga¹²

studied the process for the formation of silver colloid in photosensitive glass and measured the changes of the absorption spectrum with temperature in the range from 25 to 550°. New absorption bands with maxima at 235, 275, 360 and 412 mμ were observed. Similar absorption bands were observed by A. I. Berezhnoi and Y. M. Polukhin¹³.

The present investigation was undertaken with a view to studying systematically the effect of various factors on the nature and intensity of colour produced as well as to develop photosensitive glasses containing silver on which photographs with sharp contrast and fine details could be printed.

Experimental

Preparation of glasses: Raw materials used for making the glasses were acid washed quartz and AR grade chemicals. The glass compositions used were: N_2O 15, ZnO 10, SiO_2 75 wt per cent with Ag 0.07, CeO_2 0.05, SnO_2 0.2 gm per 100 gm of glass.

Sodium nitrate was used as an oxidising agent and sodium silicofluoride as a fining agent. Batch for 400-500 gm glass was melted in a Pt-10 per cent Rh crucible in an electric globar furnace at $1400 \pm 10^\circ$. After repeated crushing and melting, it was cast, annealed, ground and polished. The glass pieces were irradiated uniformly on both the surfaces from a 300W uv lamp at a distance of 22.8 cm. Absorption spectra of these glasses were recorded on Cary-14 recording spectrophotometer.

Results

Effect of duration of exposure: The samples of photosensitive glass were subjected to uv radiations for 15, 30, 60 and 120 minutes respectively. Absorption spectra of the samples exposed for 15 and 30 minutes were recorded before heat-treatment (Fig 1). These glasses had very strong absorption in the ultraviolet region. The glass samples after exposure to uv radiations were heat-treated at 530° for 30 minutes. Absorption spectra of these glasses possessed a strong band

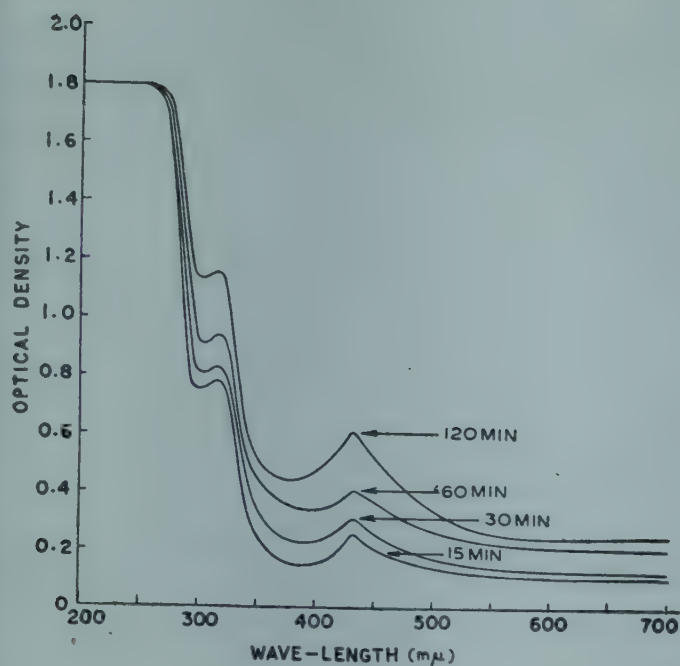


Fig 2

Effect of duration of exposure on colour. Heat-treatment at 530° for 30 min

around 315 $m\mu$ and another at about 430 $m\mu$. The visual colour of the samples changed from faint yellow to deep bright yellow with increasing duration of exposure. Optical density of colour increased with increasing duration of exposure (Fig 2).

Effect of temperature of heat-treatment: The glass pieces were exposed to uv radiations for 60 minutes and heat-treated at 450°, 500°, 530° and 550° for 30 minutes. The glass samples irradiated and heat-treated through different ranges of temperature showed one band around 315 $m\mu$ and another in the visible region which was observed at 420, 425, 430 and 430 $m\mu$ respectively for the above temperatures. The absorption spectra of these glasses showed that with increasing temperature the absorption band around 420 $m\mu$ shifted more towards the longer wavelength and the intensity of absorption increased (Fig 3).

Effect of concentration of silver: The samples of photosensitive silver yellow glasses containing 0.05 to 0.11 per cent Ag were exposed to uv radiations for 60 minutes and heat-treated at 530° for 30 minutes. The absorption curves

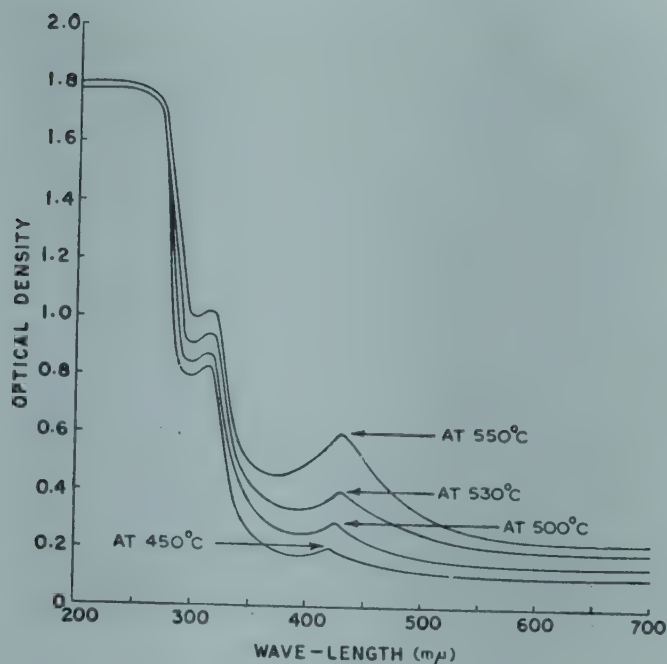


Fig 3

Effect of temperature of heat-treatment on colour. Duration of exposure—60 min; duration of heat-treatment at 530° for 30 min

(Fig 4) showed that with increasing concentration of silver, the intensity of absorption at both the maxima *ie*, at 315 $m\mu$ and 430 $m\mu$ increased without any shift in the wavelength.

Effect of concentration of sensitiser (CeO_2): The samples of photosensitive silver glasses containing 0.01 to 0.05 per cent CeO_2 were exposed to uv radiations for 60 minutes and heat-treated at 530° for 30 minutes. The intensity of absorption at both the peaks increased as the concentration of CeO_2 was increased (Fig 5). The position of the absorption maxima remained unchanged.

Electron microscopic study

Process of extraction of silver particles: The glass powder was decomposed with hydrofluoric acid which was later evaporated to dryness. After evaporation, distilled water was added and the resulting supernatant liquid was decanted off into the beaker. Thus the final product was a suspension of minute particles of silver. A drop of the suspension was placed on a previously prepared Formvar film and evaporated to dryness. The transmission micrograph as well as selected area

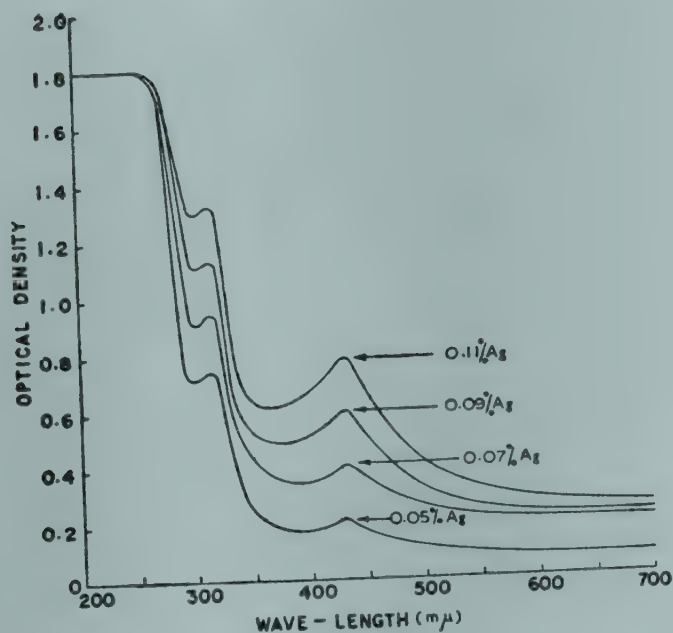


Fig 4

Effect of concentration of silver on colour. Duration of exposure—60 min; heat-treatment at 530° for 30 min

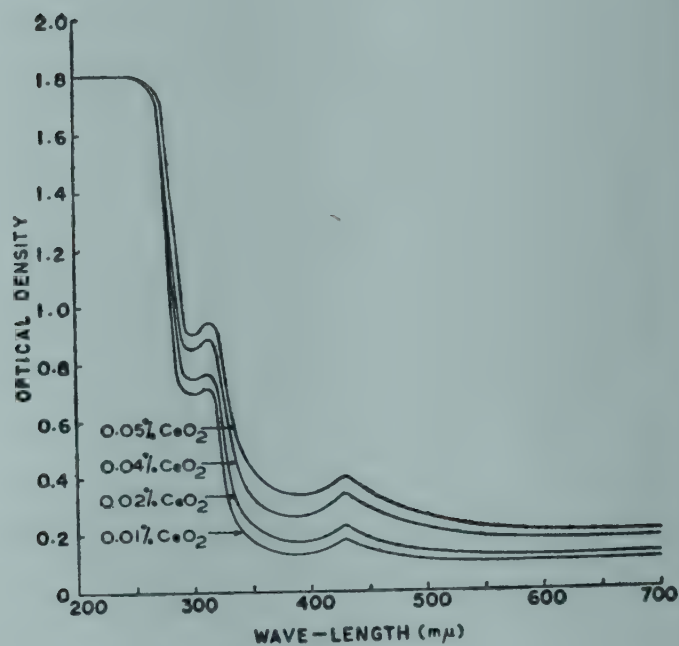


Fig 5

Effect of concentration of cerium on colour. Duration of exposure—60 min; heat-treatment at 530° for 30 min

diffraction patterns were taken on Philips EM-300 electron microscope at 80 kV.

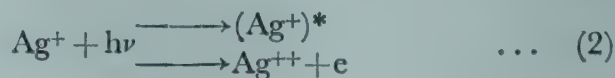
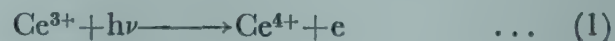
The electron micrograph of the particles revealed that the particles are uniformly distributed. They were globular in shape and 10-20 mμ in size (Fig 6). The selected area diffraction pattern of the particles (Fig 7) corresponded to a FCC (face centred cubic) lattice. As silver particles have FCC structure, the diffraction pattern was thought to be due to silver particles.

Electron microscopic study has clearly revealed the presence of colloidal silver particles of 10-20 mμ in size. The silver sols containing silver colloids in the range of 10-20 mμ are of yellow colour¹⁴. On analogy it was concluded that the yellow colour in photosensitive silver glasses was due to colloidal silver of 10-20 mμ size.

Mechanism of colour formation

When silver compounds (<2 per cent) were introduced in the glass and melted under oxidising condition, silver remained in the ionic form (Ag⁺). Hence the photosensitive glass doped with silver remained colourless. During irradiation with ultraviolet light, photoelectrons were re-

leased from the Ce³⁺ ion and the structural defects of the glass network (eqn 1). These electrons were trapped at the vacant sites of the glass lattice. The quantum of light during its interaction either excited the silver ion or oxidised it with the formation of a free electron (eqn 2). On heat-treatment, they were captured by the Ag⁺ and Ag⁺⁺ ions forming neutral silver (Ag⁰) which coagulated further and formed colloidal silver (eqns 3, 4 and 5).



The photosensitive silver glass was colourless before irradiation with ultraviolet light, but developed a faint yellow colour after irradiation with it. Its spectra showed strong absorption band in the uv region (Fig 1).

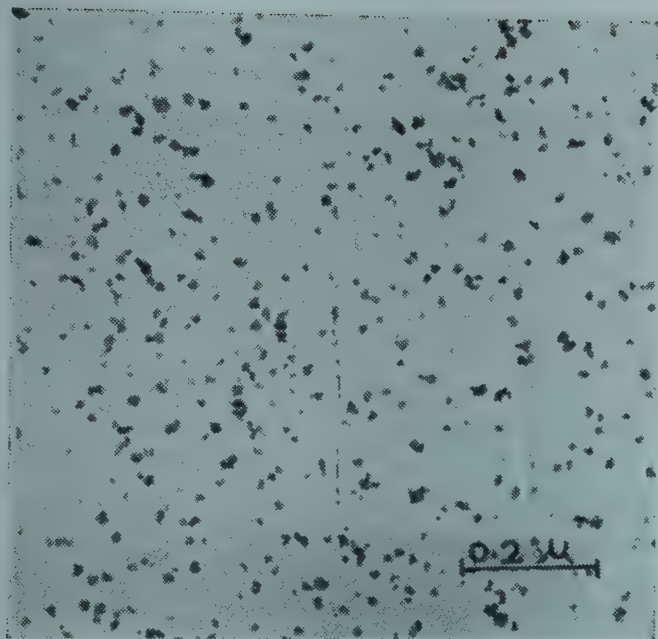


Fig 6

Electron micrograph of the extracted particles from photosensitive silver yellow glass heat-treated at 530°

Some workers^{12,15,16} have observed that on irradiating the photosensitive glasses containing silver with uv radiations, strong absorption peaks appeared in the uv region. Heat-treatment above 300° , resulted in the formation of a new peak around $405\text{ m}\mu$ with the decrease in intensity. The peak around $405\text{ m}\mu$ was attributed to the formation of colloidal silver. Irradiated glasses before heat-treatment showed strong fluorescence in the ultraviolet region which clearly indicated the presence of atomic silver. EPR and ESR⁹ studies have also indicated the presence of atomic silver in irradiated glasses. The strong absorption in the ultraviolet (Fig 1) might be due to atomic silver.

The hexavalent chromium¹⁷ is known to possess two strong absorption bands in the uv range without any peak in the visible region. The yellow colour due to Cr^{6+} ion is due to the absorption edge of uv peak extending in the visible region. Similarly the yellow colour in the irradiated photosensitive silver glass was due to the extension of the absorption edge of uv band in the visible region.

With increasing duration of exposure, the

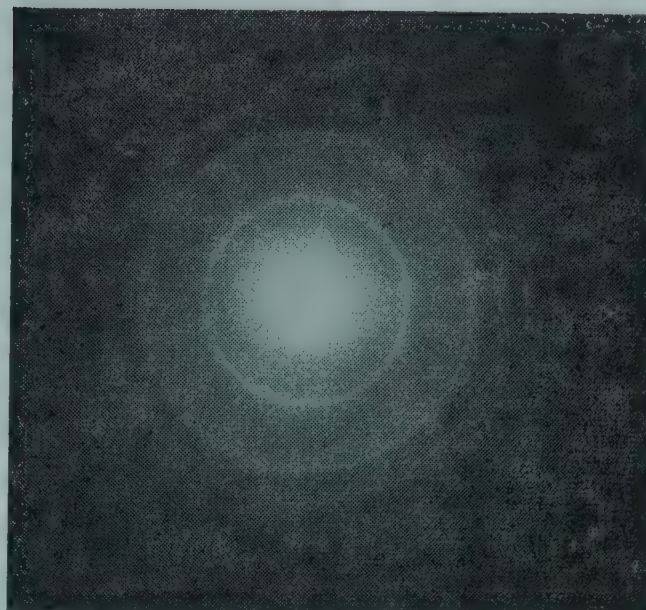


Fig 7

Diffraction pattern of the extracted particles from photosensitive silver yellow glass

number of photoelectrons released from trivalent cerium (Ce^{3+}), Ag^{+} ions and from the structural defects of the glass network, increased (eqns 1 and 3). Some electrons were trapped in vacant sites of the glass lattice whereas some interacted with Ag^{+} ions to form neutral silver (eqn 3). On heating the glass, the silver atoms coagulated to form silver colloid. At the same time electrons were liberated from their traps and neutralised Ag^{+} and Ag^{2+} ions to form neutral silver which coagulated further to form colloidal silver. As a result, permanent yellow colour appeared due to the formation of colloidal silver.

The aggregation of the particles resulted in increased intensity of colouring only when the contact of 'conglomerating' particles was so close that collectivisation of conduction electrons took place¹⁸. Hence on increasing the temperature of heat-treatment the viscosity of glasses decreased and mobility of silver particles increased which resulted in the formation of such a close contact between the colloidal particles. This was probably the reason for the increased intensity of colouring and the shift of the absorption maxima into the region of longer wavelengths.

With increasing concentration of silver ions, more of silver particles were available for coagulation to form silver colloids and as a result, the intensity of silver yellow colour increased (Fig 4).

The absence of shift of the maxima into region of longer wavelengths and the intensity of colouring might be explained by the absence of a close contact between the colloidal particles that collectivisation of conduction electrons did not take place.

Summary

Heat-treated photosensitive glasses doped with silver possessed two strong absorption peaks,

at 315 m μ and around 430 m μ . The peak at 315 m μ was due to atomic silver and that at 430 m μ was due to colloidal silver. Electron microscopic investigation revealed the presence of colloidal silver particles in the range of 10-20 m μ which agreed well with the size of silver colloids responsible for yellow colouration of silver sols. The yellow colour was attributed to the colloidal silver of 10-20 m μ size.

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FIRING CHARACTERISTICS OF SOME CLAY-GROG MIXES

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S. P. KRISHNASWAMY†

Introduction

Physico-chemical¹⁻⁴, mineralogical⁵⁻⁷ and electrical properties^{8,9} of six clays from Jammu region, both in washed and unwashed states have already been communicated by the authors. This paper forms part of the investigations in which the observations on firing characteristics, *eg*, density, porosity and shrinkage of these clays mixed with grog (1:1) in the temperature range 600-1100° are presented. An attempt has been made to study the effect of particle size and pressure on the firing characteristics of the compacts.

Experimental

The clay dried at 110° was mixed with grog calcined at 750° in equal proportions. The mixture was crushed to pass through 40, 80 and 120 ASTM sieves. Compacts of one inch cube were made using these three particle sizes at 2500, 5000, 7500 and 10,000 lbs/inch². Methods adopted to determine the firing characteristics of the specimens were the same as already reported¹⁻⁴.

Observations and discussions

Observations on the density, porosity and linear shrinkage of clay pellets fired in the temperature range 600-1100° using different particle sizes and pressures have been recorded in Tables I, II and III respectively.

Density remained constant between 600° and 700° in clay 1. In other clays, it was constant extended up to 750-800°. The constancy of the density curves (Fig 1) for pellets prepared from

—120 ASTM particle size and pressed at 10,000 lbs/inch² indicated that the loss of hydroxyl ion and accompanied changes in dimensions did not contribute towards any change in the density. All clays excepting clay 6 showed fairly steep rise in density after about 800° which continued up to 1000°, followed by a marginal rise up to 1100°. In clay 6, gradual rise in the density was observed between 800° and 1100°. The observed increase in the density was attributed to the fluxing action of alkalies and other mineral impurities present in clays.

Clay 6 gave maximum density at 1100° followed by clay 1 for compacts pressed at 10,000 lbs/inch²; whereas the minimum was observed in clay 5. Maximum density at elevated temperatures as observed in clay 6 might be attributed to the presence of high alumina in the sample. Lustre observed on the surfaces of compacts of clays 2 to 5 around 1000° indicated the presence of soluble salts which migrated to the surface. Absence of lustre in clays 1-6 suggested the possible presence of organic and vegetable matter imparting higher initial value of density in these samples. Comparatively smaller and gradual rise of the density curves of clay 6 might be attributed to the presence of quartz^{5,7} and low amount of fluxes in it.

Data obtained did not give any direct relationship between the particle size and the density. This suggested that there are some other factors also, which controlled the density characteristics of the samples.

Maximum porosity in all samples was observed at 600°. It was highest in clay 3. Beyond 600° to 700/800° there was a gradual decrease (Fig 2) which might be attributed to the expul-

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TABLE I

Density of compacts using different particle size and forming pressure (lb/inch²)

Clay	Particle size (mesh)	600°					700°					800°					900°					1000°					1100°				
		2500	5000	7500	10000	10000	2500	5000	7500	10000	10000	2500	5000	7500	10000	10000	2500	5000	7500	10000	10000	2500	5000	7500	10000	10000	2500	5000	7500	10000	10000
1	40	1.35	1.44	1.50	1.68	1.36	1.45	1.51	1.69	1.56	1.68	1.78	2.04	1.72	1.84	1.94	2.16	1.78	1.88	1.96	2.22	1.80	1.90	1.99	2.26	2.26	1.80	1.90	1.99	2.26	2.26
	80	1.21	1.33	1.44	1.56	1.22	1.34	1.44	1.57	1.60	1.76	1.87	2.02	1.76	1.86	1.96	2.13	1.80	1.90	1.98	2.17	1.84	1.92	2.00	2.21	2.21	1.84	1.92	2.00	2.21	2.21
	120	1.23	1.31	1.38	1.49	1.24	1.32	1.40	1.50	1.66	1.74	1.85	1.97	1.86	1.98	2.06	2.18	1.96	2.05	2.16	2.32	1.99	2.10	2.20	2.36	2.36	1.99	2.10	2.20	2.36	2.36
2	40	1.13	1.20	1.28	1.48	1.14	1.21	1.29	1.49	1.16	1.24	1.32	1.54	1.46	1.58	1.70	1.93	1.74	1.84	1.94	2.24	1.81	1.90	2.04	2.33	2.33	1.81	1.90	2.04	2.33	2.33
	80	1.16	1.21	1.31	1.38	1.16	1.22	1.32	1.39	1.22	1.28	1.42	1.52	1.47	1.60	1.78	1.94	1.72	1.86	1.96	2.12	1.82	1.96	2.07	2.18	2.18	1.82	1.96	2.07	2.18	2.18
	120	1.21	1.28	1.32	1.48	1.22	1.28	1.33	1.49	1.24	1.34	1.40	1.55	1.44	1.52	1.60	1.82	1.63	1.70	1.80	2.04	1.74	1.82	1.88	2.12	2.12	1.74	1.82	1.88	2.12	2.12
3	40	1.13	1.18	1.31	1.48	1.14	1.18	1.32	1.49	1.19	1.25	1.36	1.54	1.37	1.48	1.63	1.82	1.68	1.74	1.83	2.09	1.74	1.78	1.90	2.16	2.16	1.74	1.78	1.90	2.16	2.16
	80	1.15	1.32	1.38	1.50	1.16	1.32	1.38	1.50	1.22	1.36	1.46	1.60	1.56	1.78	1.89	2.03	2.00	2.14	2.20	2.30	2.08	2.21	2.29	2.42	2.42	2.08	2.21	2.29	2.42	2.42
	120	1.18	1.21	1.33	1.48	1.19	1.22	1.34	1.49	1.24	1.30	1.43	1.60	1.56	1.67	1.80	1.98	1.90	1.97	2.08	2.22	2.00	2.06	2.16	2.28	2.28	2.00	2.06	2.16	2.28	2.28
4	40	1.35	1.43	1.52	1.61	1.36	1.44	1.52	1.62	1.40	1.50	1.65	1.75	1.67	1.82	1.97	2.07	2.04	2.16	2.25	2.32	2.16	2.26	2.34	2.41	2.41	2.16	2.26	2.34	2.41	2.41
	80	1.40	1.42	1.48	1.52	1.40	1.43	1.48	1.53	1.44	1.48	1.56	1.62	1.72	1.78	1.86	1.93	2.02	2.06	2.12	2.17	2.12	2.15	2.20	2.24	2.24	2.12	2.15	2.20	2.24	2.24
	120	1.41	1.44	1.46	1.48	1.42	1.44	1.46	1.48	1.46	1.50	1.55	1.58	1.68	1.73	1.78	1.82	1.93	1.96	2.00	2.03	2.02	2.04	2.06	2.09	2.09	2.02	2.04	2.06	2.09	2.09
5	40	1.31	1.44	1.50	1.54	1.32	1.45	1.51	1.55	1.40	1.55	1.64	1.71	1.61	1.76	1.83	1.89	1.76	1.92	1.98	2.02	1.83	1.96	2.02	2.06	2.06	1.83	1.96	2.02	2.06	2.06
	80	1.30	1.42	1.45	1.54	1.31	1.42	1.46	1.54	1.45	1.61	1.67	1.80	1.73	1.88	1.92	2.08	2.00	2.08	2.12	2.28	2.06	2.12	2.15	2.32	2.32	2.06	2.12	2.15	2.32	2.32
	120	1.40	1.44	1.45	1.52	1.41	1.44	1.46	1.54	1.46	1.53	1.60	1.68	1.68	1.76	1.82	1.90	1.88	1.92	1.97	2.02	1.92	1.96	2.00	2.06	2.06	1.92	1.96	2.00	2.06	2.06
6	40	1.81	1.85	1.90	1.96	1.81	1.86	1.91	1.96	1.82	1.86	1.91	1.97	1.83	1.86	1.92	1.98	1.84	1.88	1.94	2.00	1.86	1.91	1.98	2.04	2.04	1.86	1.91	1.98	2.04	2.04
	80	1.83	1.86	1.90	1.94	1.84	1.86	1.90	1.94	1.84	1.86	1.91	1.94	1.84	1.87	1.91	1.96	1.86	1.90	1.96	2.00	1.90	1.94	2.00	2.05	2.05	1.90	1.94	2.00	2.05	2.05
	120	1.64	1.70	1.96	2.06	1.65	1.71	1.97	2.06	1.65	1.72	1.97	2.06	1.68	1.80	2.03	2.16	1.75	1.90	2.13	2.29	1.88	2.00	2.28	2.44	2.44	1.88	2.00	2.28	2.44	2.44

sion of water from the pores resulting in minor rearrangement of the pores by air. While this gradual fall was up to 700° in clays 3, 4 and 5, it extended up to 800° in clay 2 and even slightly more in clay 6, depending upon the water con-

tent in the samples. Clays 1 and 5 gave comparatively sharper fall in this region owing to higher water content. Clay 6 had least amount of water and hence the gradual fall.

The steep fall of the curves (Fig 2) around

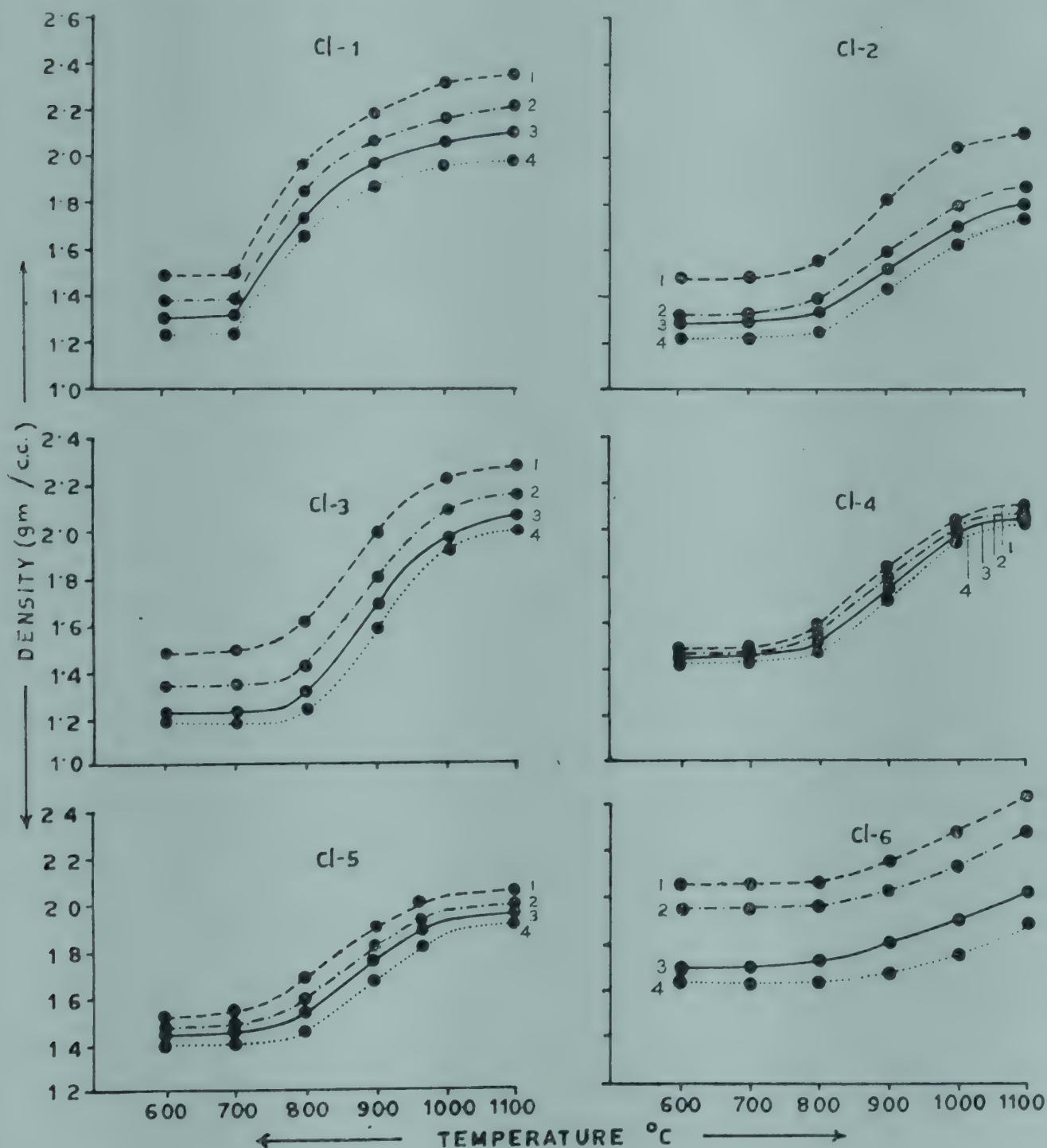


Fig 1

Temperature and pressure variation of density (clay : grog :: 1:1). 1—10,000 lbs/inch² (---), 2—7,500 lbs/inch² (- · - · -), 3—5,000 lbs/inch² (—), 4—2,500 lbs/inch² (....)

TABLE II

Porosity (%) of compacts using different particle size and forming pressure (lb/inch²)

Clay	Particle size (mesh)	600°					700°					800°					900°					1000°					1100°				
		2500	5000	7500	10000		2500	5000	7500	10000		2500	5000	7500	10000		2500	5000	7500	10000		2500	5000	7500	10000		2500	5000	7500	10000	
1	40	27.5	25.0	22.5	21.5	27.0	23.0	19.5	17.5	18.0	11.0	6.5	5.0	5.0	3.5	2.0	1.0	7.0	5.0	3.5	2.5	5.0	3.5	2.0	1.0						
	80	29.0	27.5	26.5	25.5	28.0	26.0	24.5	23.0	20.5	17.0	14.5	12.0	8.5	6.0	4.5	3.0	5.0	4.0	2.5	1.5	6.5	5.0	3.5	2.5						
	120	29.5	28.0	27.0	25.0	28.0	26.5	24.5	22.0	19.5	15.0	13.0	10.5	7.5	5.0	3.0	2.0	4.0	2.5	1.5	0.5	5.0	3.5	2.5	1.0						
2	40	32.0	31.5	30.0	25.5	31.5	31.0	29.5	29.0	31.0	29.5	28.0	26.0	23.5	19.5	17.0	15.0	9.0	7.0	5.0	4.5	1.0	0.75	0.50	0.50						
	80	35.5	34.5	33.5	32.5	35.0	34.5	33.5	32.5	34.5	33.0	32.0	29.5	30.0	27.5	25.5	21.0	15.0	13.0	10.5	8.0	1.5	1.0	1.0	0.50						
	120	35.0	34.0	33.5	32.5	34.5	34.0	33.0	32.5	34.5	34.0	33.0	31.5	31.0	29.5	28.0	24.5	14.0	12.0	10.5	7.5	1.0	0.75	0.50	0.50						
3	40	32.0	31.5	30.0	28.0	32.0	30.0	29.5	27.5	30.0	28.0	27.0	35.0	23.0	19.5	18.0	15.0	11.0	9.0	7.5	5.5	6.0	4.5	3.0	2.0						
	80	35.0	32.0	30.0	29.0	34.0	32.5	29.5	28.5	32.0	29.0	26.0	24.5	25.5	20.0	17.0	14.5	11.0	8.5	6.5	5.0	1.5	1.5	1.0	0.75						
	120	37.0	35.5	33.5	31.5	36.0	35.0	32.5	30.0	31.0	29.0	25.5	22.0	16.5	14.0	11.0	9.0	1.5	1.5	1.0	1.0	1.0	0.75	0.50	0.50						
4	40	26.5	24.5	24.0	23.5	26.0	24.5	24.0	23.0	24.0	22.5	21.0	20.0	18.0	15.5	14.0	12.5	7.0	6.0	4.5	3.0	1.5	1.0	1.0	0.75						
	80	30.5	29.0	27.0	25.5	29.5	28.5	27.0	24.5	25.5	23.0	20.5	18.0	12.5	11.0	9.0	8.0	3.5	3.0	2.0	1.5	1.0	1.0	0.75	0.50						
	120	32.5	31.0	30.5	29.5	32.0	30.5	30.0	29.0	29.0	27.0	25.0	23.5	13.5	10.5	8.5	6.5	2.0	2.0	1.5	1.5	1.0	0.75	0.50	0.25						
5	40	25.5	24.0	23.0	22.5	24.5	23.5	22.5	22.0	21.0	20.0	19.0	17.5	14.0	12.0	11.0	9.0	4.5	4.0	3.0	2.5	1.5	1.0	1.0	0.75						
	80	32.0	29.5	29.0	25.5	30.0	27.5	26.5	23.0	25.0	21.0	18.0	15.0	15.0	12.0	11.0	7.5	6.5	5.0	4.0	2.5	1.5	1.0	1.0	0.75						
	120	32.0	29.0	27.5	26.5	30.0	27.0	25.0	23.5	24.0	20.0	17.5	16.0	14.0	11.0	9.0	7.5	6.0	4.0	3.5	2.5	1.5	1.0	1.0	0.50						
6	40	23.5	22.0	21.0	20.0	23.0	22.0	20.5	19.5	22.0	20.5	19.0	18.0	18.5	16.5	15.0	14.5	12.0	10.0	8.5	8.0	4.0	2.5	2.0	1.5						
	80	26.5	24.0	22.5	21.5	25.5	24.0	22.5	21.0	25.0	23.0	22.0	20.5	22.0	19.5	17.5	16.0	14.5	12.0	10.5	9.0	5.0	4.0	2.5	2.0						
	120	27.5	26.5	25.0	24.0	27.0	26.0	25.0	24.0	27.0	25.5	24.5	23.0	25.0	24.0	22.5	21.0	16.0	14.0	12.5	10.5	7.5	6.0	5.0	4.0						

700/800° in all samples, except clay 6 in which it began at 900°, was due to the combination of alkaline fluxes with alumina and silica forming a glassy matrix. Also calcium carbonate de-

composed at such temperatures and reacted to give sharp fall in porosity. With further increase in temperature, the molten mass flowed into the pores decreasing the porosity to minimum. At

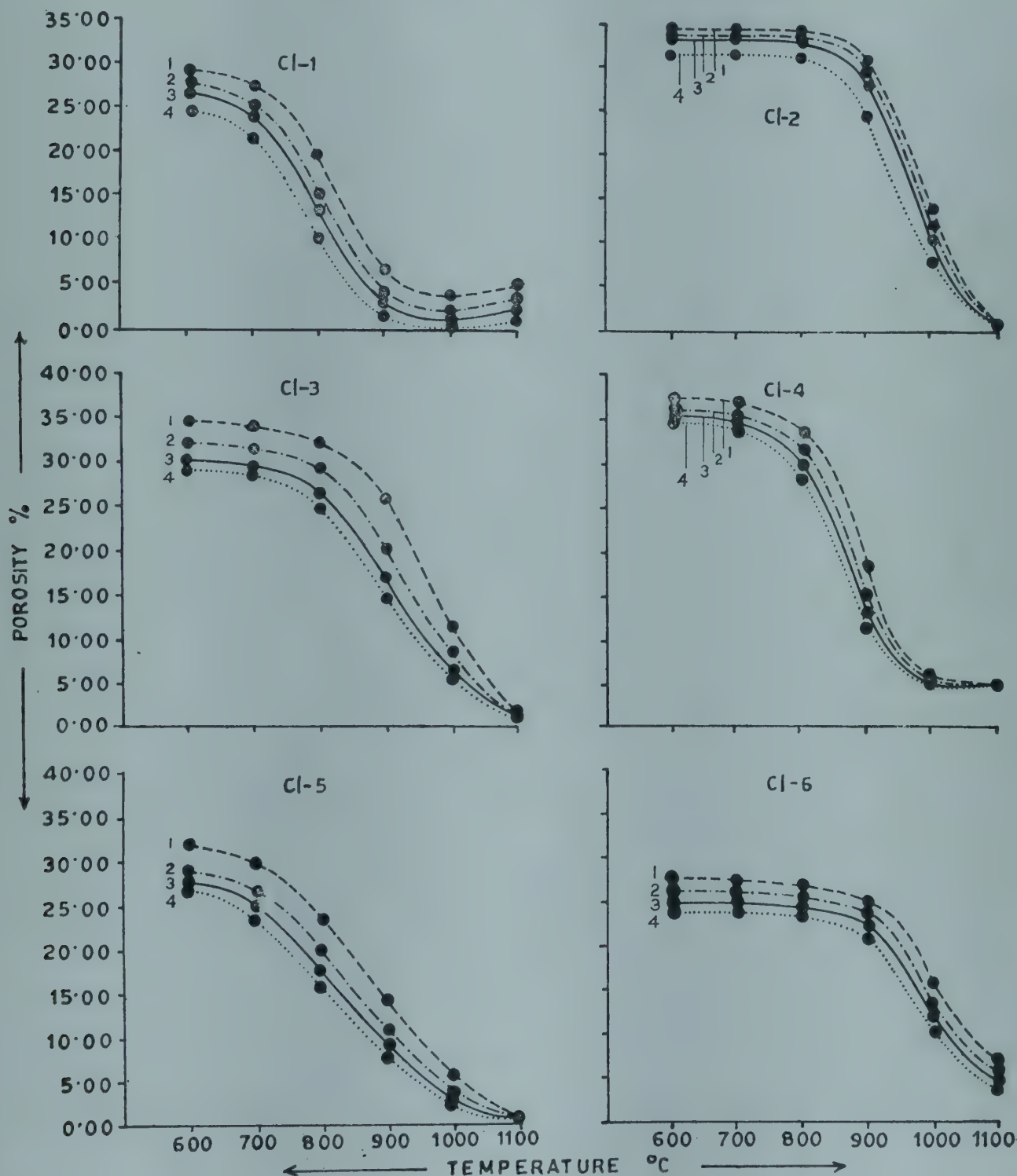


Fig 2
Temperature and pressure variation of porosity (clay : grog :: 1 : 1). 1—2,500 lbs/inch² (----), 2—5,000 lbs/inch² (- · - · -), 3—7,500 lbs/inch² (—), 4—10,000 lbs/inch² (....)

TABLE III

Linear shrinkage of compacts using different particle size and forming pressure (lb/inch²)

Clay	Particle size (mesh)	600°					700°					800°					900°					1000°					1100°				
		2500	5000	7500	10000		2500	5000	7500	10000		2500	5000	7500	10000		2500	5000	7500	10000		2500	5000	7500	10000		2500	5000	7500	10000	
1	40	.004	.003	.003	.003	.003	.003	.003	.003	.004	.155	.110	.100	.090	.190	.155	.140	.125	.200	.170	.150	.140	.200	.175	.155	.145					
	80	.004	.003	.004	.003	.003	.004	.004	.003	.003	.170	.125	.110	.100	.200	.175	.155	.140	.215	.190	.170	.160	.220	.195	.175	.160					
	120	.005	.004	.004	.004	.004	.005	.004	.005	.004	.200	.165	.125	.110	.235	.215	.196	.150	.250	.230	.215	.175	.255	.235	.220	.196					
2	40	.005	.005	.005	.004	.004	.007	.006	.005	.006	.020	.015	.010	.010	.110	.090	.080	.070	.285	.265	.225	.215	.295	.285	.255	.235					
	80	.005	.004	.005	.005	.005	.007	.006	.006	.005	.025	.020	.015	.015	.125	.105	.090	.080	.290	.265	.235	.210	.300	.285	.260	.235					
	120	.005	.005	.004	.004	.004	.010	.009	.010	.010	.025	.020	.015	.015	.130	.115	.085	.075	.285	.255	.220	.205	.300	.285	.255	.240					
3	40	.005	.004	.004	.005	.007	.007	.006	.005	.007	.040	.030	.020	.015	.135	.115	.095	.080	.035	.180	.160	.150	.240	.195	.170	.155					
	80	.007	.008	.009	.009	.009	.009	.010	.009	.010	.045	.040	.025	.020	.195	.170	.150	.135	.275	.240	.200	.185	.285	.255	.215	.190					
	120	.008	.009	.010	.009	.009	.010	.010	.010	.009	.055	.045	.035	.025	.210	.185	.165	.145	.305	.275	.245	.120	.315	.285	.255	.230					
4	40	.007	.008	.007	.006	.008	.008	.008	.009	.008	.045	.040	.035	.025	.155	.140	.125	.115	.195	.180	.165	.155	.200	.185	.175	.160					
	80	.004	.007	.008	.005	.008	.008	.008	.009	.007	.025	.020	.015	.010	.130	.120	.100	.090	.220	.200	.180	.175	.230	.210	.195	.180					
	120	.008	.007	.006	.005	.010	.010	.011	.009	.009	.030	.025	.020	.015	.135	.120	.100	.090	.230	.210	.190	.175	.240	.225	.205	.185					
5	40	.005	.007	.006	.005	.006	.006	.007	.005	.005	.025	.020	.015	.010	.135	.115	.105	.090	.160	.145	.130	.125	.165	.150	.140	.130					
	80	.009	.007	.008	.005	.009	.009	.008	.008	.007	.040	.035	.030	.015	.180	.145	.125	.100	.230	.190	.170	.155	.240	.200	.180	.165					
	120	.008	.006	.007	.006	.010	.009	.009	.009	.008	.035	.030	.020	.015	.165	.145	.120	.100	.240	.205	.175	.160	.250	.220	.200	.175					
6	40	.001	.002	.002	.002	.002	.002	.002	.002	.002	.003	.005	.002	.002	.005	.004	.004	.003	.065	.050	.035	.015	.070	.055	.045	.020					
	80	.002	.002	.003	.002	.004	.004	.004	.003	.003	.007	.006	.006	.006	.008	.008	.007	.007	.080	.070	.060	.055	.095	.080	.070	.065					
	120	.004	.004	.003	.003	.003	.005	.004	.004	.003	.008	.008	.007	.005	.010	.009	.009	.008	.100	.080	.070	.060	.115	.095	.085	.075					

this stage all the pores were completely filled and locked.

Clays 2 and 3 were sandy clays with lesser percentage of fine particles⁴. They were more porous at 600° and least at 1100°. A slight upward trend observed in clay 1 beyond 1000° indicated the bloating of the sample (Fig 2).

Increase in forming pressure resulted in decrease in porosity, as a consequence of decrease

in void space. The decrease in the particle size increased the porosity of the compact at 600°. Such a change might be due to large surface area factor. At elevated temperatures the percentage reduction in porosity of compacts with finer particle size was more, as finer particles fused readily than coarser ones.

Linear shrinkage observations (Fig 3) revealed that no change in dimensions took place up to

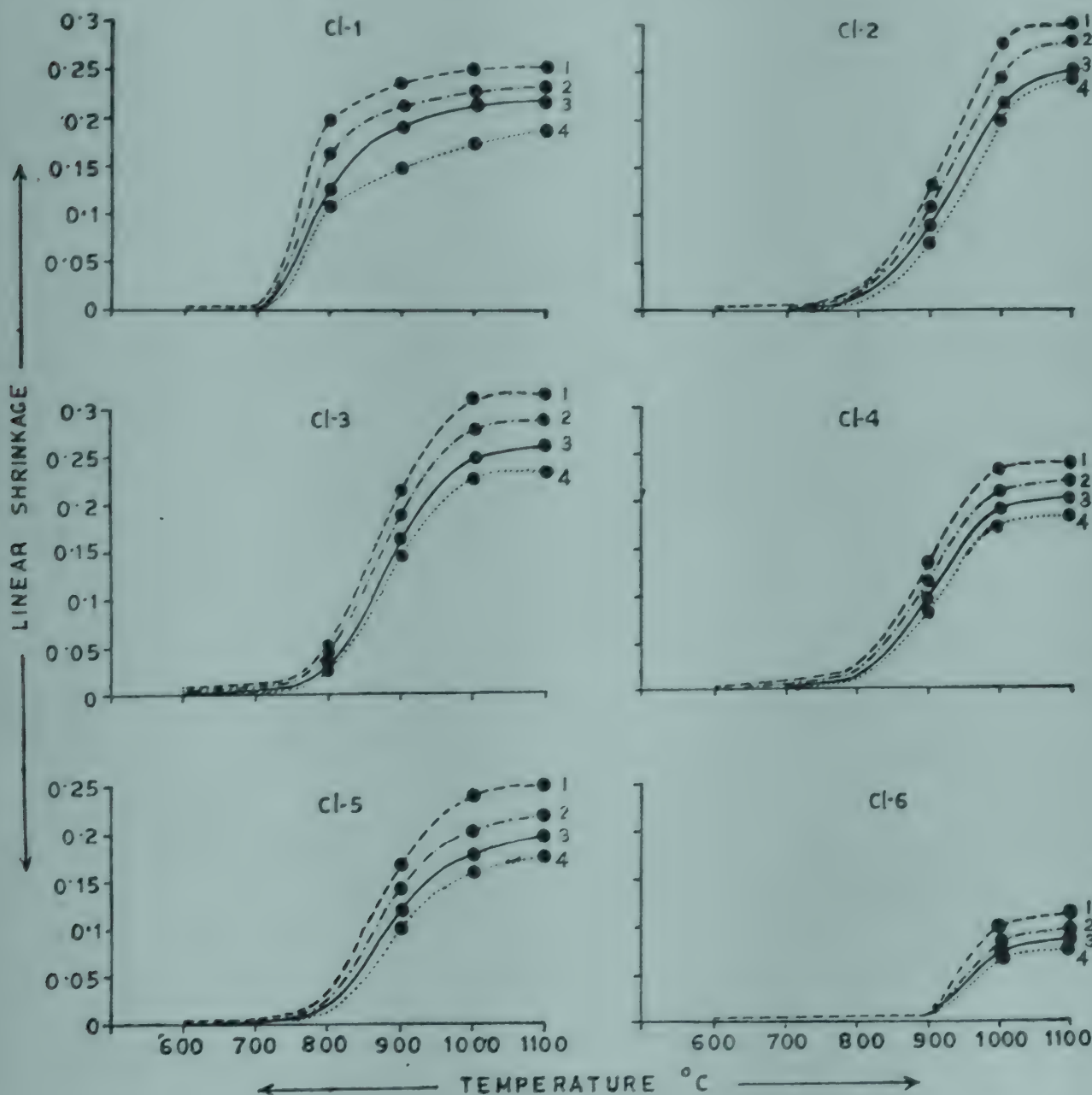


Fig 3
Temperature and pressure variation of shrinkage (clay : grog :: 1 : 1). 1-2,500 lbs/inch² (----),
2-5,000 lbs/inch² (- · - · -), 3-7,500 lbs/inch² (—), 4-10,000 lbs/inch² (....)

700-800°, except in clay 6 in which no contraction was observed even up to 900°. A large contraction beyond 700/800° might be attributed to the alkalis, the most effective fluxing agents, which combined with silica and alumina to form liquid resulting in a rapid change in dimensions. This contraction increased with the increase in liquid formation as the temperature rose. Also the sharp change between 800° and 1000° might partly be attributed to the inherent nature of clays and the presence of grog which also shrinked along with clay and contributed to the overall higher contraction of the specimens. Beyond 1000°, gradual shrinkage was observed in all the samples.

Minimum shrinkage observed in clay 6 might be due to the presence of alumina which acted as nonreactive skeleton and higher percentage of humous material, both of which reduced the firing shrinkage.

The increase in forming pressure decreased the contact points between the grains within the specimen resulting in slower shrinkage rate. The reduction in the percentage of shrinkage with particle size may also be due to the fact that finely divided material reacts much more readily

than the coarser one and, therefore, decrease in volume or shrinkage develops faster in finer samples.

Summary

Properties on firing of six Jammu clays mixed with grog were determined.

Forming pressure increased the density of the samples while it decreased the porosity and shrinkage.

No direct relationship was found between the particle size of the clays and their density after firing. However, finer particle size decreased the porosity and increased the shrinkage of the specimens.

Acknowledgment

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PHASE COMPOSITION AND REACTIONS OF SEMI-STABLE DOLOMITE REFRACTORIES

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Introduction

In Egypt, there is a wide scope for use of dolomite refractories which are relatively cheaper than magnesite.

Dolomite rock, when calcined, has a strong tendency to slake in air. This is due to the hydration and carbonisation of its content of free CaO. The process of coating calcined dolomite grains with a low melting matrix or with organic material, such as tar, or both to reduce the rate at which slaking occurs is termed semi-stabilisation process.

Semi-stable dolomite refractories contain free CaO with limited resistance to hydration when stored in air. They are generally prepared from fully shrunk sintered dolomite, by addition of a flux, and after being hard fired they are sealed from the atmosphere by soaking or mixing with tar. Essential fluxes are the oxides: SiO_2 , Al_2O_3 , Fe_2O_3 and Cr_2O_3 . One or more of these oxides could be added. In many cases, commercial materials are used as fluxes instead of pure oxides.

The aim of the present work was to study the conditions of the preparation of semi-stable dolomite refractory bodies from the Egyptian dolomite and talc-magnesite rocks; and the correlation between the determined technological properties and the mineral composition of the prepared products.

Experimental

Raw materials: The raw materials investigated

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were dolomite and talc-magnesite which occur as workable deposits in Egypt.

X-ray analysis, using spectrometer with Geiger counter technique, indicated that dolomite rock (Fig 1-A) consisted mainly of the mineral dolomite $[\text{Ca}, \text{Mg}(\text{CO}_3)_2]$. Talc-magnesite rocks (Fig 1-B) consisted mainly of the minerals magnesite (MgCO_3) and steatite ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$).

Differential thermal analysis curves, using Linseis apparatus are shown in Fig 2. Dolomite rock (Fig 2-A) showed two characteristic peaks of the mineral dolomite at 730° and 830° due to the evolution of its carbon dioxide. Talc-magnesite rock (Fig 2-B) showed two endothermic reactions (a and b) occurring at 590° and 910° respectively. The first endothermic reaction was due to the decomposition of the mineral magnesite. The second one, was due to the loss of water of constitution of the steatite mineral.

The chemical analysis of both materials is given in Table I. Results obtained indicated that dolomite rock was of high purity. The CaO/MgO ratio was close to the theoretical value of dolomite mineral (1.39), and accordingly it was suitable for preparing semi-stable dolomite refractories. Talc-magnesite rock was found to contain a reasonable amount of SiO_2 , Al_2O_3 and Fe_2O_3 which are considered as fluxing oxides. Also, it contained a relatively high amount of MgO, which caused an increase of MgO in the end product.

Preparation of semi-stable dolomite refractory bodies: Dolomite and talc-magnesite mix compositions, for preparing semi-stable dolomite pro-

ducts, could be chosen after proper understanding of the reactions that may occur during firing of these mixtures. Therefore, the study of the phase relationships for the quaternary system $\text{CaO-MgO-SiO}_2\text{-Fe}_2\text{O}_3$ (Al_2O_3), indicated by J. White² was helpful. Semi-stable dolomite refractories were found to belong to a compositional tetrahedron which has the following mineral assemblage at its corners: CaO , $3\text{CaO}\cdot\text{SiO}_2$, $(2\text{CaO}\cdot\text{Fe}_2\text{O}_3+4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3)$, and MgO , where CaO/SiO_2 molar ratio is considerably higher than 2.

Mix composition consisting of dolomite (90 per cent) and talc-magnesite (10 per cent) rocks was used for preparing the semi-stable dolomite clinker. The dolomite and talc-magnesite rocks were crushed and ground to pass 0.1

mm sieve. The proposed composition were made through intimate mixing, and then moulded in the form of cylindrical briquettes of 2.54 cm diameter under a pressure of 900 kg/cm² using the semi-dry pressing process. The moulded briquettes were dried at 110° for 24

TABLE I

Chemical analysis of the raw materials

Chemical constituents	Dolomite rock	Talc-magnesite rock
SiO_2	0.42	29.25
Fe_2O_3	0.36	6.33
Al_2O_3	0.13	1.13
CaO	30.59	1.47
MgO	20.89	34.74
Ignition loss	47.39	27.12

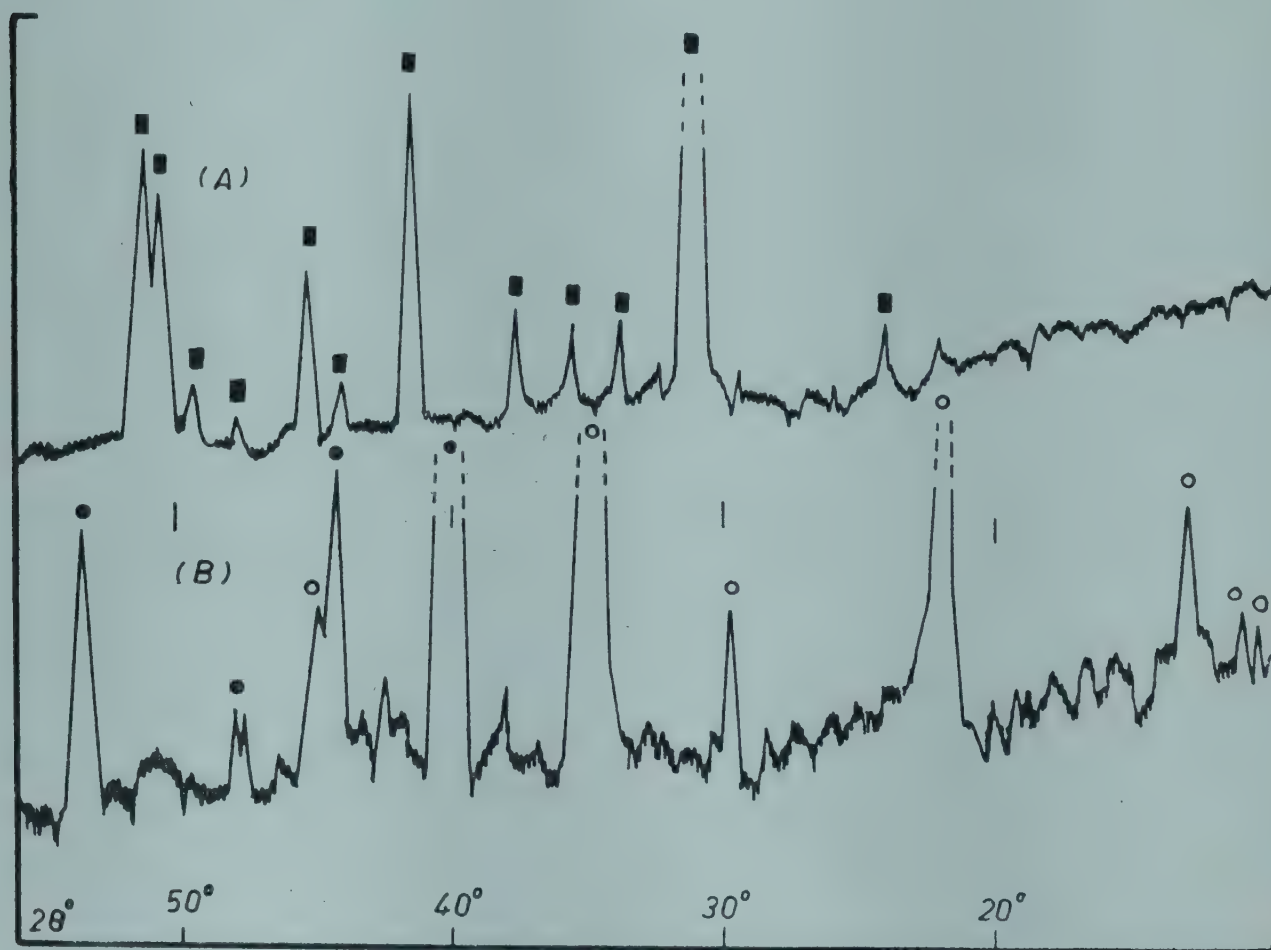


Fig 1

X-ray diffraction patterns of dolomite (curve A) and talc-magnesite (curve B): ■—dolomite, ○—talc (steatite) and ●—magnesite

hours and then fired at 1550° for 2 hours in an electric furnace with U-shaped molybdenum disilicide heating elements.

The prepared clinker was crushed, ground and classified into two grain size fractions. The first coarse fraction was between 0.8 and 0.16 mm and the second fine fraction was —0.16 mm. A series of semi-stable dolomite briquettes were made from a mixture of coarse fraction (70 per cent) and fine fraction (30 per cent), which gave the best packing results. To avoid the hydration of free CaO present, this mixture was mixed with a suitable amount of linseed oil as a binder. Briquettes were formed, dried, and

fired under the same conditions as stated above for clinker preparation.

Calculated mineral composition: The mineral components of the prepared mix fired at 1550° was found out by calculation from the data of its chemical analysis. The calculations proceeded in accordance with the equilibrium phase condensations in the system $\text{CaO-MgO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ using simple mathematical method^{2,3}. The chemical constitution of the prepared mix composition and its calculated mineral composition are represented in Table II.

Composition and properties

Mineral composition: The actual mineral composition of the prepared mix composition was determined qualitatively by means of X-ray analysis and quantitatively through special technique of rational chemical analysis.

X-ray analysis (Fig 3) showed the presence of crystalline lime (CaO) and periclase (MgO), in addition to the tricalcium silicate mineral.

The quantitative analysis of the mineral constituents was carried out by the method adopted by T.F. Korzokhina⁴ which is based on the selective solubility of the different minerals through special treatment. For each finely ground sample (—0.06 mm), five determinations

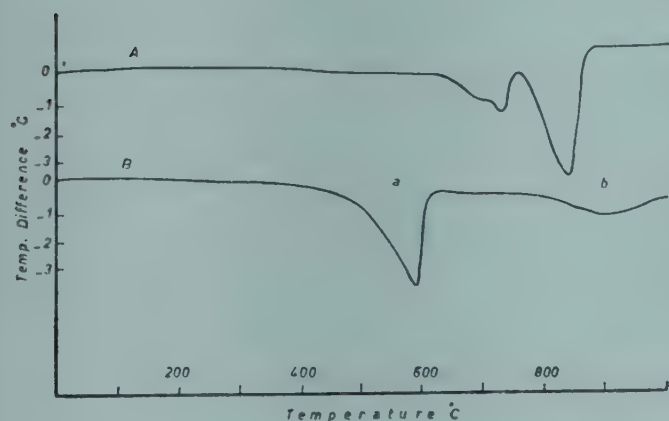


Fig 2

Dta curves of dolomite (A) and talc-magnesite (B)

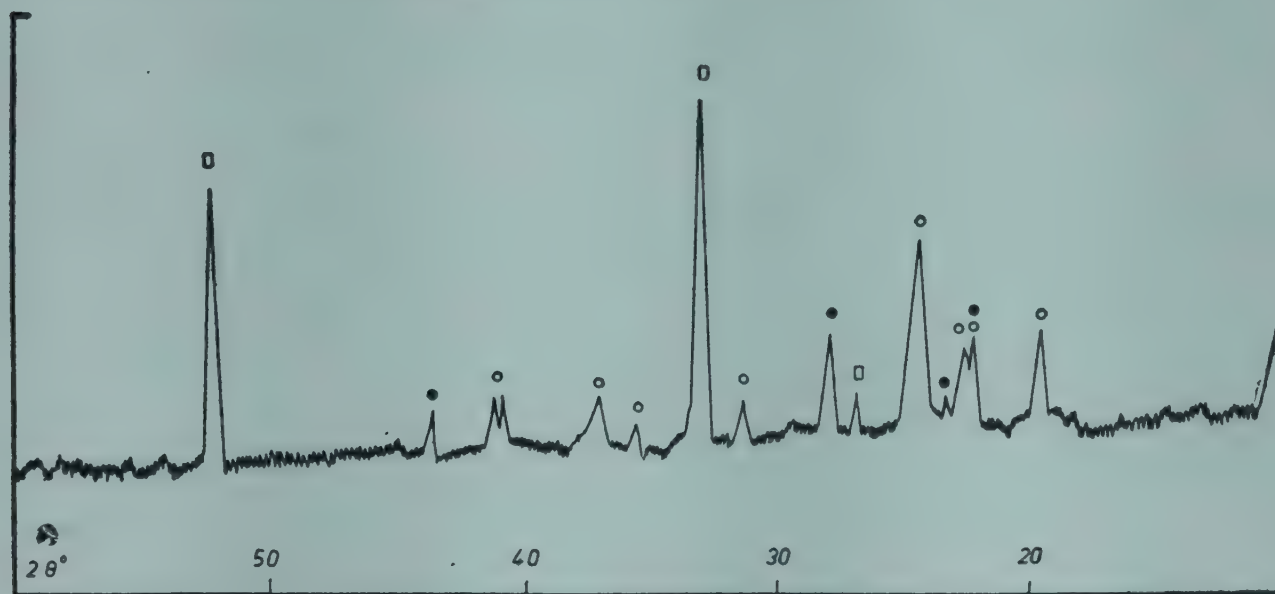


Fig 3

X-ray diffraction pattern of prepared semi-stable dolomite: ● — free CaO, ○ — C_3S and □ — free MgO

were carried out: (a) total chemical analysis of the sample¹; (b) free lime content⁵; (c) C_4AF and C_2F minerals were the only soluble minerals among the various ones comprising the sample, when the latter was treated with 20 per cent Rochelle salt (Na , K tartarate) on heating. Their content was calculated from the liberated ferric oxide and aluminium oxide in the solution; (d) C_3S and C_2S were the only soluble minerals, when the sample was treated with saturated solution of boric acid in cold and then with 5 per cent solution of sodium carbonate on heating. Their content was calculated from the liberated SiO_2 and CaO in the solution; and (e) Periclase was the only soluble mineral, when the sample was treated with 10 per cent solution of $NH_4(NO_3)_2$ and then with 5 per cent solution of Na_2CO_3 , on heating. Its content was calculated from the liberated MgO in the solution.

Tables III and IV show the results obtained at the different steps of the method together with the final mineral proportions. The difference in two parallel determinations of each mineral shown in Table IV, lies usually within the limits of 0.5 per cent.

Properties: The physical and refractory properties of the end product shown in Table V, were determined by British Standard testing procedures⁶. The results were found to comply with the standard international specifications.

TABLE II

Chemical constitution of the prepared semi-stable dolomite mix composition and its calculated mineral composition

Chemical constitution of the fired mix		Calculated mineral composition	
Constituents	Per cent	Minerals	Wt per cent
SiO_2	6.24	Tricalcium silicate (C_3S)	23.71
Fe_2O_3	1.70	Brown millierite (C_4AF)	2.00
Al_2O_3	0.42	Dicalcium ferrite (C_2F)	1.77
CaO	50.98	Free lime (CaO)	31.86
MgO	40.62	Periclase (MgO)	40.62

Discussion

The normal semi-stable dolomite material should have the following chemical composition⁷: CaO 48-50, MgO 36-40, SiO_2 3-5, Fe_2O_3 1-3 and Al_2O_3 1-3 wt per cent.

Pure dolomite is extremely difficult to sinter and gives approximately 15 per cent porosity after heating at 1700° . A temperature of 1800° is necessary to produce sintered bodies. Such temperature is not considered as practical in industry. In practice, fluxes are added to accelerate sintering so that it may occur at a relatively lower temperature.

The Egyptian dolomite used in the present work was found of high purity. Therefore, 10 per cent of talc-magnesite rock was added to the dolomite for preparing semi-stable dolomite clinker. A clinker consisting mainly of crystalline CaO and periclase was produced by firing this mixture at 1550° for 2 hours. During this process relatively smaller amount of CaO reacted with SiO_2 to form tricalcium silicate (C_3S) and with the limited amount of Fe_2O_3 and Al_2O_3 to form a solid solution of brown-millierite and dicalcium ferrite ($C_4AF + C_2F$).

The prepared semi-stable dolomite clinker remained firm and resisted hydration in air for a long period (more than one year). Such clinker when crushed and reformed using water as binder, hydrated and crumbled whilst drying. This indicated that the 10 per cent talc-magnesite

TABLE III

Composition of the prepared semi-stable dolomite mix

Method	Components of mix 1				
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO
Chem analysis (%)	6.24	1.70	0.42	50.98	40.62
Free lime (%)	—	—	—	31.90	—
Fe_2O_3 and Al_2O_3 by Rochelle salt (%)	—	1.69	0.42	—	—
SiO_2 and CaO by boric acid (%)	6.21	—	—	17.50	—
MgO by $NH_4(NO_3)_2$ solution (%)	—	—	—	—	40.48

TABLE IV

Mineral constituents of the prepared semi-stable dolomite mix composition

Minerals	SiO ₂		Fe ₂ O ₃		Al ₂ O ₃		CaO		MgO		Mineral constituents	
	Per cent	Mol wt ratio	Per cent	Mol wt ratio	Per cent	Mol wt ratio	Per cent	Mol wt ratio	Per cent	Mol wt ratio	Determined	Calculated
CaO	—	—	—	—	—	—	31.90	0.570	—	—	31.90	31.86
C ₃ S	6.21	0.1035	—	—	—	—	17.39	0.3105	—	—	23.60	23.71
C ₄ AF	—	—	0.66	0.0041	0.42	0.0041	0.92	0.0164	—	—	2.00	2.00
C ₂ F	—	—	1.03	0.0064	—	—	0.72	0.0128	—	—	1.75	1.77
MgO	—	—	—	—	—	—	—	—	40.48	1.012	40.48	40.62

C=CaO; S=SiO₂; F=Fe₂O₃; A=Al₂O₃ and M=MgO

TABLE V

Physical and refractory properties of the prepared semi-stable dolomite products

Properties	Investigated semi-stable dolomite brick	British semi-stable dolomite brick
Bulk density (gm/ml)	2.82	2.52
Apparent porosity (%)	14.40	22.80
Cold crushing strength (kg/cm ²)	1250	260
Permanent linear change on reheating for 2 hours at 1550° (%)	—0.70	—1.2
Refractoriness under load	under a load of 2 kg/cm ²	under a load of 3.5 kg/cm ²
Rising temp test:		
Initial softening (°C)	1650	1360
Failure, >10% subsidence (°C)	>1700	1610
Thermal shock resistance (cycles)	30+	23

bond added had formed a silicate and aluminoferrite coating around the dolomite grains, and as soon as this coating was broken, the samples proceeded to hydration. Therefore, linseed oil

was used instead of water as a binder for the preparation of semi-stable dolomite briquettes from the graded clinker.

The prepared semi-stable dolomite consisted mainly of the high melting crystalline CaO, periclase and C₃S, in addition to a solid solution of the low melting compounds C₄AF and C₂F, which formed the matrix of the end product. If the quantity of matrix minerals was high, the refractory properties of the end product, at operating conditions, was low. If it was too small, sintering process became difficult.

The presence of suitable amount (3.75 per cent) of the low melting matrix minerals C₄AF + C₂F did not affect the refractory properties of the end product. Also, the enhanced recrystallisation and crystal growth of the main constituents CaO and periclase led to high bonding strength at high temperature⁸.

Such products showed high refractoriness (>1850°) and their subsidence under a load of 2 kg/cm² started at 1550°. A failure did not occur up to 1700°. At the same time, the prepared bodies showed good sinterability.

The results (Table IV) show close agreement between the mineral composition determined experimentally and that calculated from thermal equilibrium data, thus confirming that the re-

actions in the fired products approached the equilibrium state.

Summary

Good quality semi-stable dolomite refractory product could be obtained through addition of 10 per cent talc magnesite rock to the dolomite, on firing at relatively lower temperature of 1550° for 2 hours. The end product was hard, sintered, volume stable, containing high amount of free lime and could be stored for a long time. It

showed high refractoriness and high resistance to subsidence under load. Such characteristics were very important for its resistance to erosion by slags in actual use. The prepared bodies could be safely used for lining the heating zone of rotary kilns used in firing of dolomite, limestone and portland cement, in place of magnesite refractories. Such product when mixed with tar, could also be used for lining Bessemer converters, basic open hearth bottoms, basic electric furnace bottoms and LD converters.

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(Ms received April 15, 1976)

RESEARCH NOTE

LOW TEMPERATURE RED CLAY GLAZES*

Ordinary red clay articles start fusing at about 1000° and so glazes meant for red clay pottery should mature below that temperature. The coefficient of expansion of red clay bodies are very low and so the glaze should have a coefficient of expansion equal to or below that of the body to develop a compressive layer. Low temperature maturing glazes are generally fritted. It is very difficult to make a raw glaze maturing at a low temperature and secondly, low fusing glaze materials are water soluble and as such require fritting to make them insoluble. Lead oxide if used in these glazes requires to be fritted to make it insoluble so that it is less injurious to human health.

Frit batch compositions of one transparent and one opaque glaze are given in Table I. Zircon sand which is easily available is used as opacifier. Zircon sand is first ground fine to pass 300 mesh sieve, magnetted, washed and then dried for use as opacifier in frit batch. Mill batch (in both the cases) consists of frit 95 and china clay 5 wt per cent. Maturing temperature of the glazes are between 850° and 900°.

The batch materials are mixed thoroughly by sieving and then smelted in a suitable frit furnace at about 1280-1300° in oxidising atmosphere and granulated in water. After the frit is dried, mill batch is charged with china clay as suspending agent. The glaze is wet ground

TABLE I

Frit-batch compositions of transparent and opaque glazes

Composition (wt per cent)	Transparent glaze	Opaque glaze
Felspar	30	27
Quartz	33	29
Red lead	6	6
Borax	10	18
Boric acid	15	6
Barium carbonate	6	6
Ground zircon sand	—	8

to pass 250 mesh sieve and magnetted to remove free iron, if any. The specific gravity of the glaze slurry is to be adjusted according to the absorption property of the biscuited ware to be glazed.

After finishing, the glazed wares are fired in a muffle furnace at a temperature range 850-900° with soaking of one hour at the peak temperature. The schedule of firing may be between 12-15 hours. The transparent glaze is also suitable for underglaze colour developments. The on-glaze colours may also be used on both the glazes.

The developed glazes have the following properties: (i) glaze maturing range 50-75°, (ii) soluble lead—less than 2 ppm, (iii) gloss—good, and (iv) cost of glaze (1976 basis)—Rs 3000.00 per tonne (approximately).

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THERMAL DECOMPOSITION OF RAJASTHAN LEPIDOLITE*

Introduction

Occurrence of lepidolite in India has been reported from Bihar, Madhya Pradesh and Rajasthan. In Rajasthan, lepidolite occurs as an accessory mineral in some granite porphyries. The mineral is used in glass and ceramic industries. Ceramic bodies containing lithium oxide have very low coefficient of thermal expansion and high thermal shock resistance. S. K. Das and R. L. Thakur¹ developed a number of compositions for ceramised glasses using lepidolite and spodumene. They also developed machinable glass-ceramics from glasses utilising lepidolite. A number of workers²⁻⁵ have studied the thermal decomposition of micas. R. Roy² studied the heat-treatment of lepidolite between 900° and 1000°. He observed the formation of a phase which he called para lepidolite. E. K. Cundy *et al*³ studied the effect of heat-treatment on zinnwaldite, a lithium-iron bearing mica and found that at 1000° the crystalline structure of the mineral disappeared.

In this communication the results of thermal decomposition of lepidolite from Rajasthan are reported.

Experimental

Beneficiation of the sample: Lepidolite from Rajasthan consisted of small flaky particles having dia usually not exceeding 2 mm. Associated with it were a few quartz like spherical particles of 0.1 mm dia which disintegrated by pressing with nails. After disintegration these showed a flake like morphology under magnifying glass.

The material was beneficiated by crushing it on a clean steel plate by rolling a steel cylinder

over it. Crushed material was then passed through a 100 mesh sieve. The fraction above 100 mesh sieve was collected. This was washed several times with distilled water and subsequently dried in an air oven between 80° and 100°.

Results and discussions

X-ray, dta and chemical analyses: X-ray diffraction of the samples was done and their 'd' values are given (Table I). The results of chemical

TABLE I

Lattice spacings of Rajasthan lepidolite

dÅ	Intensity (I/I ₁)	dÅ	Intensity (I/I ₁)
10.5	VW	2.45	6b
9.5	VW	2.38	6b
5.0	1	2.24	5b
4.5	7	2.17	Wb
4.3	Spotted	2.13	5b
4.1	Spotted	2.01	Spotted
3.9	8	1.96	Spotted
3.72	8	1.801	VW
3.48	8	1.742	VW
3.34	8	1.710	VW
3.20	8	1.680	VW
2.99	6	1.630	3
2.85	5	1.550	VVW
2.78	4	1.540	VVW
2.58	10	1.490	10b
2.55	10		

VW-very weak, b-broad, Wb-weak and broad, VVW-very very weak

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analyses show to contain SiO_2 —51.52, Al_2O_3 —25.94, Fe_2O_3 —0.42, Li_2O —3.37, K_2O —10.10, Na_2O —0.97, CaO —0.27, MgO —0.39, F—4.64 per cent and LOI—4.50 per cent at 1000° . Dta curve is shown in Fig 1.

The average diameters of the particles of lepidolite used for heat-treatment were 1 to 2 mm. The samples were heated at three different temperatures (900° , 1000° and 1100°) for one hour. Dta curve showed that the mineral completely decomposed at 900° . Table II shows the 'd' values from X-ray diffraction of the samples heated at

TABLE II

X-ray analysis of heat-treated lepidolite

Observed 'd' values	Leucite (K, AlSi_2O_6) ASTM data card 15-47	Assigned lithium aluminium silicate ^{8,9}
Intensity (I/I_1) dÅ	dÅ Intensity (I/I_1)	
—	9.5	40
—	6.6	14
W	5.55	50
S	5.39	80
W	4.75	40
5	4.50	—
—	4.335	20
—	3.784	30
VVW	3.60	40
10	3.49	35
8	3.41	85
Spotted	3.32	—
9	3.25	100
—	3.217	8
—	3.159	8
—	3.090	35
—	3.043	30
4	2.92	70
4	2.82	70
4	2.80	55
—	2.685	8
2	2.62	40
2	2.60	20
—	2.487	30
4	2.35	65
—	2.329	30
—	2.308	30
4	2.26	8
—	2.192	8
—	2.162	30
VW	2.12	50
VW	2.08	—
—	2.065	30
VW	2.01	20
—	1.980	8
VVW	1.96	—

W-weak, S-strong, VVW-very very weak, VW-very weak

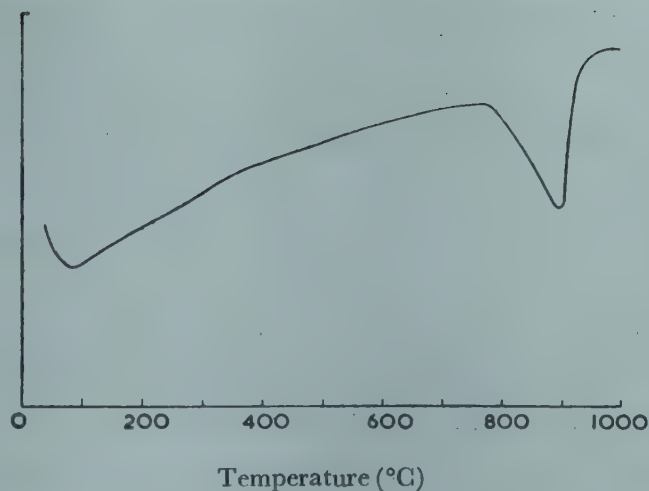


Fig 1

Dta curve of lepidolite run at a heating rate of $10^\circ/\text{min}$

1100° . The lines obtained could be assigned to leucite. By comparing with ASTM data cards it was seen that many weaker lines did not appear in the diffraction diagram. It was seen that some of the lines consistently had smaller 'd' values than reported in ASTM data cards. These could be due to change in unit cell dimension caused by a slight change in the composition of the mineral. A few of the lines could not be unambiguously identified. It was thought that these lines were due to stuffed β -quartz type of structure⁶⁻⁸ of composition lithium-aluminium silicate. In β -quartz (high) structure smaller sized ions like Li^+ , Mg^{2+} can be accommodated in the voids of the lattice⁷. E. R. Segnit and T. Gelb⁸ reported that Li^+ , Mg^{2+} , Fe^{2+} , Zn^{2+} and Cu^{2+} with ionic radii 0.66 to 0.77 Å could go in solid solution. It is likely that in the present case, besides the formation of leucite, lithium-aluminium-silicate⁹ with β -quartz structure was obtained after the heat-treatment of lepidolite. It was not possible to assign the quantitative analysis of lithium-aluminium-silicate. It is also felt that the X-ray data of E. K. Cundy *et al*³ of heat-treated zinnwaldite was due to the formation of β -quartz stuffed derivative structure.

Summary

Thermal decomposition characteristics of lepi-

dolite from Rajasthan were investigated. Besides formation of leucite, lithium-aluminium-silicate with β -quartz structure was obtained after heat-treatment between 900° and 1100°.

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(Ms received May 8, 1977)

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CENTRAL GLASS AND CERAMIC RESEARCH INSTITUTE BULLETIN

Vol 24, No 4, 1977

Studies in bioceramics: Vitreous coatings on stainless steel needles for use as implants in reversible contraceptive device. S. K. Das, M. C. Ghose and S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (4) 99-103 (1977).

Investigations were carried out on biocompatible vitreous enamel and bioglass coating compositions for stainless steel needles for use as implant material in a reversible male contraceptive device. Vanadium bearing coatings were not found to be biocompatible whereas vanadium free and bioglass coatings were found to be fairly acceptable to the animal system.

Bioglass composition has the basic advantage of adequate stabilisation of the implant by tissue in-growth.

Mineralogy and ceramic properties of two plastic clays from Kerala. S. N. Ghosh and S. K. Guha, *Cent Glass Ceram Res Inst Bull*, **24** (4) 104-112 (1977).

Ceramic properties of Padappakara and Kumbalam clays from Trivandrum district, Kerala, were studied. Kumbalam clay was comparatively free from the associated non-clayey impurities. Padappakara clay contained free quartz and marcasite.

Padappakara and Kumbalam clays showed high plasticity. Padappakara clay can be a very good substitute for ball clay. Kumbalam clay may be used in the crude form where the fired colour is not of much importance.

Hypersensitivity of the neodymium absorption spectra in lead borate glasses. H. A. El-Batal, A. L. Hussein and A. F. Abbas, *Cent Glass Ceram Res Inst Bull*, **24** (4) 112-115 (1977).

Absorption spectra of the neodymium doped lead borate glasses showed marked splitting of the bands into several component peaks. Increase in the content of lead oxide resulted in triple splitting of the band around 350 m μ and overlapping of the weak band at 400 m μ . Addition of divalent metal oxide also showed similar splitting of the bands around 350 m μ . Substitution of PbO by divalent metal oxides caused variations in intensities of the absorption band

Thermal expansion studies on glasses of the system $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$. N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **24** (4) 116-121 (1977).

Thermal expansion studies on glasses of the system $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ were carried out by differential dilatometric measurements.

The change in coefficient of expansion of the glass with the increase of added oxide content was discussed in relation to the mode of vibration of the atoms or groups in the network, the polarisation of the ions, the mobility of the constituent ions and the ability of some cations to build glass forming units.

CENTRAL GLASS AND CERAMIC RESEARCH INSTITUTE BULLETIN

Vol 24, No 4, 1977

Etudes de biocéramique: revêtements vitreux sur les aiguilles en acier inox destinées à utiliser comme implants dans les dispositifs réversibles anticonceptuels. S. K. Das, M. C. Ghose et S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (4) 99-103 (1977).

On étudie les compositions de l'émail biocompatible et de revêtement de bio-verre pour les aiguilles en acier inox en vue d'utiliser comme du matériel d'implant dans un dispositif anticonceptuel chez le mâle. On constate que les revêtements en vanadium ne sont pas biocompatibles tandis que les revêtements sans vanadium ainsi que les revêtements de bio-verre sont assez acceptables dans l'organisme animale.

La composition de bio-verre a l'avantage fondamental d'assurer les implants d'être suffisamment stable dans le tissu qui pousse là-dedans.

Minéralogie et propriétés céramiques de deux argiles plastiques provenant de Kerala. S. N. Ghosh et S. K. Guha, *Cent Glass Ceram Res Inst Bull*, **24** (4) 104-112 (1977).

Les auteurs étudient dans cet article les propriétés céramiques des argiles provenant de Padappakara et de Kumbalam de la région de Trivandrum, Kerala. L'argile provenant de Kumbalam est relativement exempte des impuretés non argileuses qui s'y trouvent ordinairement associées. L'argile de Padappakara contient du quartz libre et de la marcassite.

Les argiles provenant de Padappakara et de Kumbalam présentent une plasticité élevée. L'argile de Padappakara peut se substituer à la ball clay. On peut utiliser l'argile de Kumbalam à la forme brute ou la couleur due à cuisson n'a pas assez d'importance.

Hypersensibilité des spectres d'absorption du néodyme dans les verres de borate au plomb. H. A. El-Batal, A. L. Hussein et A. F. Abbas, *Cent Glass Ceram Res Inst Bull*, **24** (4) 112-115 (1977).

Les spectres d'absorption des verres de borate au plomb dopés au néodyme présente des bandes bien résolues en plusieurs crochets constituants. L'augmentation de la teneur en oxyde de plomb produit de bande à trois crochets aux environs de 350 m μ et du chevauchement de la bande faible à 400 m μ . L'addition de l'oxyde métallique bivalent aussi présente de séparation semblable des bandes

aux environs de 350 m μ . La substitution de PbO par les oxydes métalliques bivalents produit des variations d'intensités de la bande d'absorption.

Etudes de la dilatation thermique des verres du système $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$. N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **24** (4) 116-121 (1977).

On étudie dans cet article la dilatation thermique des verres du système $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ au moyen des mesures différentiels dilatométriques.

On discute de l'influence de l'augmentation de la teneur en oxyde ajouté dans le système sur le coefficient de dilatation du verre en relation avec le mode de vibration des atomes ou des groupes dans le réseau, la polarisation et la mobilité des ions constituants et l'aptitude de quelques cations de former le verre.

CENTRAL GLASS AND CERAMIC RESEARCH INSTITUTE BULLETIN

Vol 24, No 4, 1977

Untersuchungen an Biokeramik: Glasartiger Farbenüberzug auf korrosionsbeständige Stahl-Nadeln zur Verwendung als Einsetzung in umkehrbarer Empfängnisverhütungsvorrichtung. S. K. Das, M. C. Ghose und S. S. Verma, *Cent Glass Ceram Res Inst Bull*, **24** (4) 99-103 (1977).

Untersuchungen wurden durchgeführt an bioverträgliches Farbemail und Bioglas Überzugzusammensetzungen für korrosionsbeständige Stahl-Nadeln zum Gebrauch als Einsetzungsmaterial in einer umkehrbaren Männer-Empfängnisverhütungsvorrichtung. Vanadiumhaltende Überzüge waren ungeeignet als bioverträgliche Stoffe, während Vanadium-freie Überzüge und Bioglas als ganz annehmbare Stoffe für das tierische System gefunden wurden.

Bioglaszusammensetzungen haben den Grundvorteil von ausreichender Stabilisierung der Einsetzung durch Gewebewachstum.

Mineralogie und keramische Eigenschaften von zwei bildfähigen Töne. S. N. Ghosh und S. K. Guha, *Cent Glass Ceram Res Inst Bull*, **24** (4) 104-112 (1977).

Keramische Eigenschaften von Töne aus Padappakara und Kumbalam Gegend des Trivandrum Bezirks, Kerala, wurden untersucht. Der Ton aus Kumbalam war vergleichmässig frei von begleitenden nichttönigen Verunreinigungen. Der Ton aus Padappakara enthielt freies Quarz und Markasit.

Die Töne aus Padappakara und Kumbalam zeigten hohe Plastizität. Der Ton aus Padappakara kann als ein sehr guter Ersatz von Bindeton benutzt werden. Der Ton

aus Kumbalam kann in den Grob benutzt werden, wenn die beheizte Farbe keine wichtige Rolle spielt.

Überempfindlichkeit von Neodymium-Absorptionsstreifen in Blei-Borat Gläser. H. A. El-Batal, A. L. Hussein und A. F. Abbas, *Cent Glass Ceram Res Inst Bull*, **24** (4) 112-115 (1977).

Absorptionsstreifen von Neodymium-dotierten Blei-Borat Gläsern zeigten starke Aufspaltung der Streifen in verschiedenen Komponent-Spitzen. Steigerung des Bleioxid-Inhalts ermöglichte eine dreimalige Aufspaltung der Streife um 350 m μ und Überdeckung der schwachen Streife bei 400 m μ . Zugabe von zweiwertiges Metalloxid auch zeigte ähnliche Aufspaltung der Streifen um 350 m μ . Ersetzung von PbO durch zweiwertiges Metalloxid verursachte Änderungen in der Intensität der Absorptionsstreifen.

Wärmeausdehnungsuntersuchungen an Gläser vom System $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$. N. A. Ghoneim, *Cent Glass Ceram Res Inst Bull*, **24** (4) 116-121 (1977).

Wärmeausdehnungsuntersuchungen an Gläser vom System $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ wurden mit Hilfe der Differentialdilatométrisch-Messungen durchgeführt.

Die Änderung in Ausdehnungskoeffizient mit der Steigerung vom zugegebenen Oxid-Inhalt wurde in Verhältnis zu der Wirkungsweise von Schwingungen der Atomen oder Gruppen im Gitter, der Polarisierung der Ionen, der Beweglichkeit der Komponente-Ionen und Fähigkeit einiger Kationen die Glasbildende-Einheiten einzubauen.

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STUDIES IN BIOCERAMICS : VITREOUS COATINGS ON STAINLESS STEEL NEEDLES FOR USE AS IMPLANTS IN REVERSIBLE CONTRACEPTIVE DEVICE

S. K. DAS, M. C. GHOSE AND S. S. VERMA*

Introduction

The concept of attaching prosthetic device to living tissue by means of tissue in-growth into porous structure is of recent origin. Work to date with medical uses of ceramics has been primarily directed towards bone prostheses and it has been shown that porous ceramics, unlike metals and medical polymers, allow for attachment and anchoring of body tissue¹. The increased surface area associated with porous materials provides a scaffolding into which tissue will grow and thus anchor the porous body to the living tissue and at the same time distribute the mechanical load over a large area and avoid the problem of local stress concentration. Investigations on porous metallic implants have also shown that the problem of corrosion is enhanced when the metals are used in porous forms². The most recent development is the application of bio-compatible ceramic coating firmly bonded to metallic devices³. The metallic parts satisfy the requirement of strength and the porous ceramic coatings provide interfacial stability of attachment by tissue in-growth. This paper represents research and development work carried out at this Institute for developing porous ceramic coatings on stainless steel needles which form a part of the reversible contraceptive device for eventual implantation in human male system.

Reversible contraceptive device

In vasectomy, the vas deferens transporting spermatozoa from the testis is cut and the cut ends are tied. The major limitation of the technique is that surgical restoration of the patency of the vas deferens is not practicable. This produces adverse psychological effect for general acceptance of this method of contraception. In recent years considerable effort has been directed towards devising convenient technique for a reversible obstruction of the passage of spermatozoa in the vas deferens.

S. K. Guha *et al*⁴ have recently made a feasibility study of the reversible blockage device (Fig 1) of the passage of spermatozoa in the vas deferens.

The body of the blockage device are made of a teflon plunger with inlet and outlet tubes that are required to be inserted into the vas deferens are made of fine needles of stainless steel. By moving the central plunger up and down, the connection

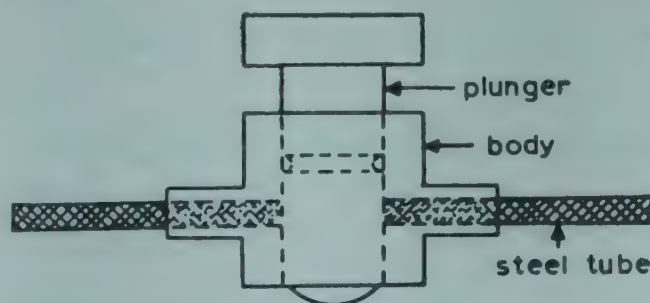


Fig 1
Reversible blockage device

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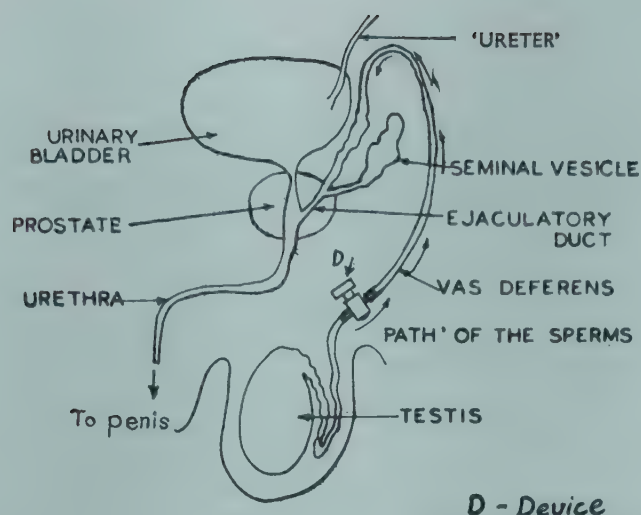


Fig 2

Location of blockage device in vas deferens of the male reproductive system

between the tubes can be cut off or maintained. The entire device is totally implanted and the inlet and outlet tubes are retained in the distal segments of vas deferens (Fig 2). It has been shown experimentally that such a device, with optimal design and dimension parameters, is feasible⁴. The ultimate failure of the device is due to the dislocation of the implant. Even knots of non-absorbable polymer threads do not prevent dislocation of the implant. To overcome this problem, a porous ceramic coating firmly bonded to the inlet and outlet tubes is thought to provide tissue in-growth around the tubes for stability of attachment.

Experimental

Laboratory scale trials were carried out with 1-2 kg batch meltings in an oil fired furnace and standard practice was followed in respect of frit making and milling for preparing the enamel slips.

Oxide compositions, fritting temperatures, mill additions, firing temperatures for different enamel frits have been studied during this investigation (Table I). Stainless steel injection needles (no 23 and no 24 of external diameter 0.5 and 0.46 mm) were used for experimental work and these were cleaned by sandblasting. The adherence of the coating appeared to be

less when the needles were pickled in hydrofluoric acid solution (5 per cent).

After application of the enamel either by dipping or spraying process, the coated needles were dried at about 100° in an electric oven and then fired in an electric muffle furnace by placing them in suitably designed jigs. A second coating of the same enamel was then applied on the first coating and again fired.

Results and discussion

The four enamel compositions BC-1 to BC-4 (Table I) produced a glossy coating finish with a blackish grey appearance and without any surface defect when applied on stainless steel needles. In order to produce a porous coating finish, a number of pore producing agents like whiting, charcoal, asbestos and aluminium metal powders were tried in the mill additions of these enamel frits. It was found that fine asbestos powder (5 per cent) or aluminium metal powder (12 per cent) produced a matt coating finish with a degree of porosity when the firing of the enamels on the needles was done under controlled conditions of temperature and soaking time. However, such firing schedule for producing a degree of porosity in the coating finish was not found sufficient for developing fully satisfactory adherence of the coating.

The biocompatibility of the coating materials was evaluated at the Indian Institute of Technology and All India Institute of Medical Sciences, New Delhi, by accelerated *in vitro* screening test and actual implantation in animal body. *In vitro* screening test was performed by exposing the coated needle to the action of a pseudo-extracellular fluid and then injecting a sample of this fluid into an experimental animal so as to determine any adverse effects. In actual implantation test, the coated stainless steel injection needles were cut into several portions with a diamond blade and a small part of the coating from one end of each of the small portions was stripped off. The bare portion of the needle thus formed was then

TABLE I
Data relating to frit compositions

Constituents	Composition (wt per cent)				
	BC-1	BC-2	BC-3	BC-4	BC-5
SiO ₂	55.00	50.50	49.00	51.00	43.00
TiO ₂	7.50	7.00	—	—	—
CaF ₂	—	—	8.00	8.00	16.00
Al ₂ O ₃	3.00	3.00	6.00	5.50	—
B ₂ O ₃	3.00	2.50	13.00	16.00	—
CaO	4.50	4.00	—	—	11.00
CoO	—	—	0.50	—	—
CuO	—	—	1.00	1.00	—
MnO ₂	—	—	0.50	—	—
V ₂ O ₅	8.80	16.00	—	—	—
P ₂ O ₅	—	—	—	—	7.00
KNaO	18.20	17.00	22.00	18.50	23.00
Fritting temperature (°C)	1450	1450	1250	1250	1200
Mill additions					
Clay	5	5	5	5	5
Borax	1	1	1	1	—
Bentonite	0.5	0.5	0.5	0.5	0.5
Water	40	40	40	40	40
Firing temperature (°C)	900	900	850	850	750

pushed into the two ends of the teflon plunger to form the implant device which was ultimately inserted into the vas deferens of sexually mature rats and rhesus monkeys.

The coating materials resulting from the compositions BC-1 and BC-2 (Table I) along with the asbestos or aluminium metal powder as pore producing agents in the mill addition were stated to be not acceptable to the body of rats. *In vitro* screening test showed toxicity effect in the nervous system resulting in a condition similar to paralysis. This indicated that a leaching of a toxic material occurred in the

pseudo-interstitial fluid, the ionic concentration of which approximately corresponded to 0.9 per cent NaCl solution.

The porous coating materials resulting from the compositions BC-3 and BC-4 (Table I) together with the asbestos or aluminium metal powder in the mill addition were reported to be fairly satisfactory in the body of rats and even in monkeys. In actual implantation test, it was reported that the degree of porosity of the coating finish caused some surface adhesion in the animal system but did not provide adequate stabilisation of the implant by tissue in-growth

into the pores of the coating. Such effect might be attributed to the possible absence of interconnection between the pores.

It has been established that bioglasses which undergo controlled surface reactions in body fluid are primarily composed of Na_2O - CaO - SiO_2 and P_2O_5 in suitable ranges of composition. These are biocompatible with living bone and are commonly used for implants³. Electron spectroscopic studies show that after implantation of such materials in body fluid, a silica rich gel film is formed on the surface of the glass due to

loss of sodium ion. Thereafter, a calcium phosphate rich layer is developed within and on top of silica rich layer⁵. With progressively longer periods of implantation (about three weeks), some in-growth of collagen fibril begin to form at the ceramic-bone interface and it continues until a complete union of the implant and the bone is made.

Composition BC-5 (Table I) is a type of bioglass which produced a matt coating finish and fairly good adherence on stainless steel needles on firing at 750° for 3-5 minutes. Electron microscopic studies of the bioglass coated needles were made before implantation in rats and also 14 days after implantation. To check up the effect of corrosion of the coating material in the interstitial fluid having an ionic concentration corresponding approximately to 0.9 per cent NaCl solution, electron microscopic studies were also made on the coated needles after dipping them in saline water. Fig 3 showed electron photomicrograph of the bioglass coated needles before implantation. It showed the porous character of the bioglass surface with some interconnecting pores. Fig 4 showed that there was not much change in the surface when the bioglass surface was dipped in saline water. Fig 5 showed a marked

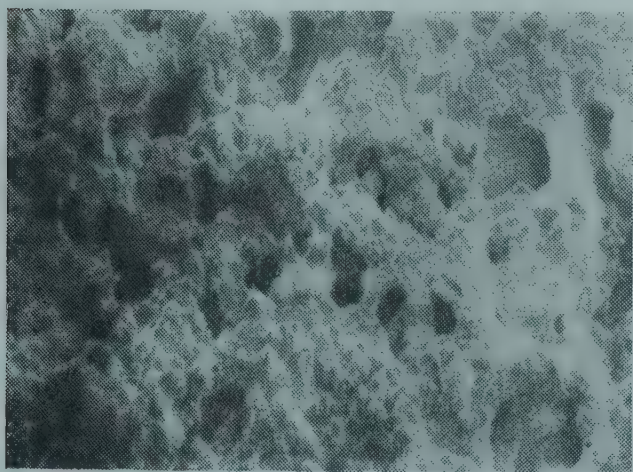


Fig 3

Scanning electron micrograph of bioglass surface showing porous character with some interconnecting pores ($\times 500$)

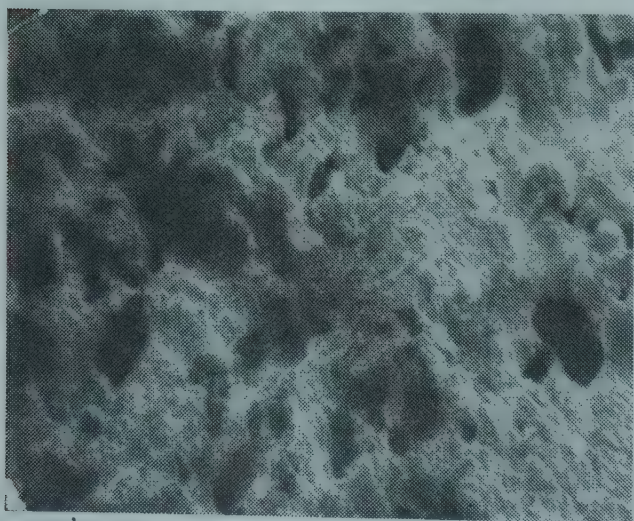


Fig 4

Scanning electron micrograph of the surface character of the bioglass showing not much change after saline dip ($\times 500$)

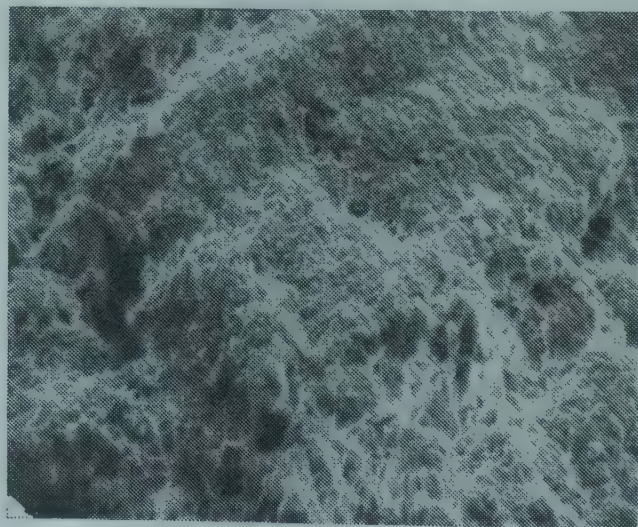


Fig 5

Scanning electron micrograph of the surface character of the bioglass showing marked change after implantation in rats for 14 days due to tissue in-growth ($\times 500$)

change of surface character caused due to the in-growth of tissue into the surface of the bioglass after implantation of the blockage device in rats for 14 days.

The results emerging from this investigation are no doubt very promising. Statistical evaluation of a large number of implant samples with the same type of bioceramic coating using a large number of different animals is required. The adherence of the bioceramic coating on the stainless steel needles is also crucial for successful stabilisation of the implant and the possibility of further improvement in the adherence of the coating particularly on small diameter injection needles is also to be explored.

Summary

The vanadium bearing coatings on the stainless steel needles as tested on rats were not found to be biocompatible due to the resulting toxicity in the animal nervous system.

The vanadium free coatings as tested on rats and rhesus monkeys were found to be nontoxic

and fairly acceptable to the animal system but the pores developed by using aluminium metal powder or asbestos powder were not interconnected resulting in inadequate tissue in-growth.

The bioglass coatings were found to be acceptable to animal bodies (rats and rhesus monkeys) and also showed adequate tissue in-growth which results in better stability of attachment of the implant and other advantages.

Acknowledgment

The authors thank Shri K. D. Sharma, Director of the Institute, for his keen interest in this work and for his kind permission to publish this paper. The authors also thank Dr S. K. Guha and Dr H. Kaur of All India Institute of Medical Sciences and Indian Institute of Technology, New Delhi, for carrying out biocompatibility tests of the coating materials and for preparing scanning electron photomicrograph and their interpretation.

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(Ms received June 5, 1977)

MINERALOGY AND CERAMIC PROPERTIES OF TWO PLASTIC CLAYS FROM KERALA

S. N. GHOSH AND S. K. GUHA*

Introduction

In view of the importance of plastic clays, especially in the pottery industry, the Central Glass and Ceramic Research Institute had undertaken a number of systematic investigations on Indian plastic clays available in the different regions of the country. S. N. Ghosh *et al*¹, made physico-chemical and mineralogical studies on seventeen plastic clays of India with the primary objective of assessing their suitability as substitute for ball clays. In the course of interaction with the Directorates of Geology and Mining of the different states, two clays from Kerala were found to be very promising, particularly in respect of their plasticity and other associated ceramic properties. The present paper deals with the mineralogy and ceramic properties of the two clays from Kerala.

The two clays included in the studies are: (i) Padappakara clay and (ii) Kumbalam clay. The deposit of Padappakara clay is located at the north shore of Padappakara Peninsula in the north of Kundara in Trivandrum district. Nearest railway station is Kundara and the deposit is approachable by good motorable road. The deposit of Kumbalam clay is located in the western end of Kumbalam ($8^{\circ}59'30''$: $76^{\circ}39'45''$), two miles north of Kundara in Trivandrum district. This deposit also is situated near Kundara railway station and is approachable by good motorable road.

Both the deposits have been described as sedimentary clays (tertiary) associated with soft

sandstones and lignite bearing ochreous clays; quality varying from ochreous and impure ferruginous material to carbonaceous varieties often with numerous small nodules strikes of marcasites and pyrites. The thickness of the deposit is 2 to 5 m covering an area of about 500 acres.

Experimental

The methods of tests adopted in this investigation were similar to those specified in ASTM².

The required quantity of representative material in each case was obtained out of a bulk supply of about one tonne of crude by adopting the standard method of coning and quartering.³ Both the clays were in the form of lumps and as such the sampling was done after crushing the same to small pieces.

Raw colour and visible impurities: The dry raw samples before grinding were visually examined for colour and impurities like quartz or sand or any other gritty matters, *eg*, mica, lignite or vegetable matter. While noting the colour, the dominant visible colour was mainly considered and all attempt was made to assign the colours, as far as possible, on the basis of the colour charts given in IS:5-1949 for ready mixed paints.

Slaking nature: The representative lumps of crude clay, about 1 inch size, were put in clear water in a beaker and the time required for complete slaking of the lumps was recorded as measure of the slaking behaviour.

According to N. Plumber and J. F. Romary⁴, the result of a slaking test was indicative of the

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binding strength of the clay particles, the ease with which they could be dispersed and the degree of consolidation of the clay aggregated mass.

Wet sieve analysis: The representative dry raw sample was crushed in a pestle mortar and sieved through 20 mesh Tyler sieve. 200 gm of the sieved material mixed with 1 litre of water was taken in a cylindrical glass jar of 2 litre capacity, allowed to slake for 2 hours and then blunged for 10 minutes in a Mitchel mixer with three-bladed propeller, 2 inch dia, at a speed of approximately 1700 rpm. The blunged material was transferred to a 325 mesh Tyler sieve and washed thoroughly by means of a small jet of water. The washing continued till a clear wash was obtained. The residue was then fractionated by passing through 100, 150, 250 and 325 mesh Tyler sieves. The residue retained on sieves was washed thoroughly, dried at 105-110°, weighed and per cent residue on individual sieve was calculated. After visually examining the nature of the dried residue, its ignition loss was determined after igniting on a Fisher burner and the nature of the ignited residue was also noted.

Plasticity by hand feel: The sample was crushed and passed through 60 mesh Tyler sieve. It was then mixed with sufficient water to form a soft mass, covered with a wet cloth and was allowed to soak for 24 hours. The plasticity of the mass was determined by hand feel after proper mixing of the mass.

Atterberg's number: The Atterberg's number was determined as the difference between the proportion of water required to produce a mass at the liquid limit² (ASTM: D423-54T) and that at plastic limit² (ASTM: D424-54T) of consistency.

Water of plasticity: The plastic mass, prepared for noting plasticity by hand feel, was used for the determination of water of plasticity according to the usual method of noting the per cent loss on drying at 110°.

Dry linear shrinkage: After the discs (made by plastic pressing) were dried in the oven at 110° and cooled in the desiccator, the distance be-

tween the shrinkage marks (originally 25 mm apart) was measured and the per cent dry linear shrinkage was calculated.

Tests on fired samples: For measuring dry shrinkage and fired properties, 30 mm dia and about 10 mm thick discs were taken. The discs, properly marked, were then placed on porcelain tiles. Shrinkage marks were put 25 mm apart along the diameter and covered with wet cloth for slow drying at room temperature so as to avoid any warpage or cracking. The air dried discs were then placed in an electric oven and the temperature gradually raised in about 6 hours to 100° and maintained overnight at that temperature. The samples were then cooled in a desiccator.

Fired colour: The samples of dry test pieces were fired in an oxidising atmosphere of an electrically heated muffle furnace at 1250° and 1400° and the colour was noted as in the case of raw sample. Appearance of any coloured specks, spots or patches was also noted.

Fired linear shrinkage: The total fired shrinkage at 1250° and 1400° was measured similarly as dry linear shrinkage.

Water absorption: Water absorption of the fired sample was determined on the same specimens as were used for colour determination. The specimens were boiled in water for 2 hours, the weight of such a 'saturated' specimen in air was taken as W, the weight of a dry specimen in air was taken as D; then the per cent water absorption was given by $[(W-D)/D] \times 100$.

Vitrification characteristics: The degree of vitrification of fired test pieces was also visually examined and categorised as high, fair, slight and no vitrification.

PCE value: The pyrometric cone equivalent of the samples was determined according to the method given in IS: 485-1953. The tests were conducted in Hirsch type carbon resistance furnace.

Chemical analysis: The method adopted for the ultimate chemical analysis of the—100 mesh material was similar to that given in the ASTM Standard methods for chemical analysis of

ceramic whiteware clays², designation C 323-537. The alkalies were determined by the Beckman flame spectrophotometer.

Rational analysis: The calculation of rational analysis from ultimate chemical analysis was done according to the Norm method illustrated by A.I. Andrews⁵. The alkalies were considered to be present as feldspathic matter.

pH measurement: The pH values of 1:5 suspension of the clays in distilled water were determined on a Cambridge pH meter by using a glass electrode. The clay suspension was prepared by mixing 20 gm of dry clay (—200 mesh Tyler sieve) with 100 ml of air bubbled distilled water and shaking the mix for 24 hours in a mechanical shaker.

Base exchange capacity: The method of determination of bec was similar to that described by S. K. Guha and S. Sen⁶ with some modifications. Only 0.5 gm of oven dried sample (—200 mesh Tyler sieve) was used and the ammonia taken up from the normal solution of ammonium acetate was distilled off with 0.5 gm MgO, absorbed in 40 per cent boric acid solution and titrated against a standard H₂SO₄ solution using a mixed indicator. The bec in me per 100 gm of clay was calculated from the titre value.

Differential thermal analysis: The apparatus used for dta tests was the same as described by Atma Ram *et al*⁷. The rate of rise of temperature of the furnace was 10° per minute up to a limit of 1000°. A micromax controller and recorder was used in operating the furnace. The dta curve was recorded on a speedomax recorder.

X-ray diffraction analysis: X-ray diffraction patterns of the clays were taken in a Guiner focussing camera provided with a quartz crystal monochromator. Philips PW-1010 X-ray crystallographic unit fitted with a copper target was used. The tube was run at 28 kV 12 mA. Time of exposure was 6 hours. Intensity I/I_1 was estimated visually with respect to the strongest line of each pattern taken as '10'.

Particle size distribution: The particle size of clays were determined by Andreasen pipette

method based on Stoke's law of sedimentation. The clay was dispersed in water containing sodium pyrophosphate as a deflocculant, in a mechanical shaker and then it was transferred to a graduated pipette for undisturbed settling. A measured quantity of suspension was drawn off at certain intervals, without disturbing the suspension. Assuming the cubical shape of the particles, the average width of the particles was considered to be 1.612 times the radius obtained from Stoke's equation.

Processing

The crude samples of both the clays were found to contain some quartz and undesirable ferruginous gritty matter. They were washed by usual clay washing method for effective removal of these impurities.

The crude clay lumps being quick slaking in nature, the sample as received was directly put into a blunger, slaked with water for one hour, blunged thoroughly for half an hour and after complete dispersion, the clay slurry at about 5 per cent suspension was allowed to flow through the experimental clay levigation unit available at the Institute. The silicious and gritty matter were thus separated out by sedimentation in the 'sand tanks' and in 'mica channels' of the levigation unit. The fine clay suspension was then screened through a 325 mesh Tyler sieve, passed through an electromagnet and finally collected in a settling tank where it was allowed to settle for 24 hours. The clear supernatant water was decanted out, the clay recovered and dried at 80-90°. The crude clay was thus fractionated into two fractions, fine clay collected in the settling tank and the residue comprising all the sediments mixed together.

Results and discussion

The raw colour of the sample as received from Padappakara was greyish white and that from Kumbalam was very light grey. They did not show any visible impurities. The crude lumps were fairly hard but they slaked quickly in water which indicated that they would not require

any crushing or grinding for dispersion in water.

Results of the wet sieve analysis and the nature of the sieve fractions after ignition at 1000° are given in Table I. The results showed that a considerable amount of grit was present in Padappakara crude and they existed in different mesh size. Total grit on 325 mesh Tyler sieve (+45 μ) was more than 14 per cent, consisting mainly of quartz with considerable proportion of black particles. The ignition test showed that the black coloured particles were mainly ferruginous type of impurities and should be responsible for development of undesirable fired specks. The colouring grits and also the maximum amount of free quartz were removed by suitable processing to improve the property of Padappakara clay and to make the clay more suitable for whiteware industry. The grit content in Kumbalam clay was much less (about 5 per cent on 325 mesh) in comparison to Padappakara clay and with minor amount of colouring grits. Also, in case of Kumbalam clay it would be possible to remove the major portion of colouring grits simply by sieving through a 150 mesh sieve and thus separating out the grits which were above 106 μ in size.

Chemical analysis, rational analysis and PCE of the clays are given in Table II. The chemical

analysis (Table II) of Padappakara clay showed that the crude clay was high in SiO₂ content (55.82 per cent) and low in alumina (28.93 per cent) and alkali (0.18 per cent). The colouring oxide (Fe₂O₃+TiO₂) content was 2.59 per cent which was likely to deteriorate the fired colour and CaO being present only in traces, chances of partial bleaching of colour due to Fe₂O₃ and TiO₂ was also less. In the processed clay, SiO₂ content had been reduced to 47.63 per cent which showed that a considerable proportion of free quartz had been removed by processing and increasing thereby the percentage of Al₂O₃ content to 34.58 per cent. The colouring oxide (Fe₂O₃+TiO₂) content in processed clay was almost the same as in crude clay indicating thereby that they existed in the clay not only in the form of coarser grit but also in finely divided state which could not be eliminated by simple water levigation.

The crude Kumbalam clay was more or less similar to processed Padappakara clay in chemical composition except in fact that Fe₂O₃ and TiO₂ content in the former was slightly on the higher side. The carbon content in both Padappakara and Kumbalam clay was generally low and, therefore, it should not have any significant effect on the property of the clays.

The mineralogical composition as obtained

TABLE I
Wet sieve analysis (Tyler standard sieves)

Particles	Microns	Padappakara		Kumbalam	
		Per cent	Nature after ignition	Per cent	Nature after ignition
On 100 mesh	150	4.8	Mainly quartz with considerable proportion of buff and black particles. LOI 19 per cent	1.5	Quartz with a few brown particles. LOI 8.37 per cent
Through 100 mesh and on 150 mesh	Between 150 and 106	2.2	Quartz with sufficient brown and black particles. LOI 1.97 per cent	0.7	—
Through 150 mesh and on 250 mesh	Between 106 and 53	3.8	Nature same as above. LOI 2.71 per cent	1.2	Quartz with negligible amount of brown particles
Through 250 mesh and on 325 mesh	Between 53 and 45	3.4	Nature same as above. LOI 6.40 per cent	1.8	Same as above

TABLE II

*Chemical analysis, rational analysis and
PCE value of the clays*

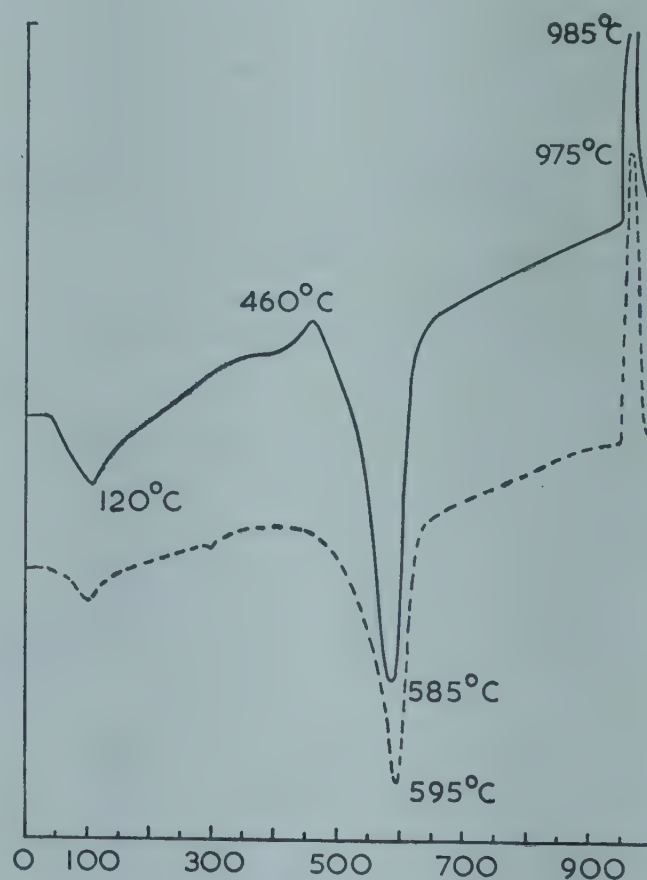
Constituent (per cent)	Padappakara		Kumbalam
	Crude	Processed	Crude
<i>Chemical analysis</i>			
SiO ₂	55.82	47.63	48.26
Al ₂ O ₃	28.93	34.58	34.00
Fe ₂ O ₃	1.28	1.30	1.84
TiO ₂	1.31	1.30	1.66
CaO	Trace	Trace	Trace
MgO	0.40	0.38	0.31
K ₂ O	0.04	0.08	0.08
Na ₂ O	0.14	0.62	0.06
LOI	11.98	13.82	13.80
Carbon	0.47	0.25	0.80
<i>Rational analysis</i>			
Kaolinite	73.42	86.06	84.98
Feldspathic matter	1.52	6.05	1.19
Hematite	1.28	1.30	1.84
Magnesite	0.83	0.79	0.65
Free quartz	21.63	4.33	8.33
Carbonaceous matter	1.45	1.32	1.55
<i>PCE value</i>			
(Orton cone)	Above 33	—	33-34 (very close to 34)

from rational analysis showed (Table II) that the crude Padappakara clay contained only 73.42 per cent kaolinite and this low kaolinite content was mainly due to the presence of as high as 21.63 per cent of free quartz. The minerals other than kaolinite and free quartz present in the clay were all in minor amount. The appreciable increase in kaolinite content (86.06 per cent) in the processed Padappakara clay was evidently due to the substantial elimination of free quartz in processing. The figures showed that more than 17 per cent of free quartz

had been separated out due to processing. The higher percentage of feldspathic matter (6.05 per cent) in the processed clay may be due to the concentration of such minerals happened by the removal of free quartz. The Kumbalam clay on the other hand contained about 85 per cent of kaolinite and more than 8 per cent of free quartz and the other minerals were present in minor amounts.

The PCE value of both Padappakara and Kumbalam clays varied between Orton cone 33 (1750°) and Orton cone 34 (1770°) which showed that the refractoriness of the clays were quite high. The Padappakara clay, in spite of its very high free quartz content showed high PCE value mainly due to the low content of feldspathic matter and other fluxing agents.

The dta curves of two clays are given in Fig I. The peak temperatures as obtained

**Fig 1**

Dta curve of Padappakara clay (—) and
Kumbalam clay (.....)

therefrom are shown in Table III. The general nature of the main endothermic and exothermic peaks showed that both Padappakara and Kumbalam clays were essentially kaolinitic in character. The size of the low temperature endothermic peaks clearly indicates that the two clays were either very fine grained or might contain in very small quantities illitic clay minerals. The presence of sharp exothermic peak at 460° in case of Padappakara clay was clearly indicative of either marcasite or pyrite. The absence of such a peak in case of Kumbalam, therefore, showed the clay comparatively free from such impurities. The remaining features of the dta curves of the two clays are in complete conformity with those of a standard kaolinitic clay.

The X-ray diffraction patterns of the two plastic clays and the relative intensity of the X-ray diffraction rings I/I_1 and the interplanar spacings d , as given in Table IIIA suggested that both the clays contain kaolinite as the predominant clay mineral. The patterns also clearly indicate the fine grained nature of the two clays showing in addition the presence of quartz as nonclayee impurity. Kumbalam clay was more fine grained than Padappakara clay from relatively more broadness of the lines in the diffraction pattern of the clay.

Particle size distribution, base exchange capacity and pH values of the two Kerala clays are given in Table IV. The data showed that the particle size distribution in processed Padappakara clay was not very much different from that in crude Kumbalam clay. In processed Padappa-

TABLE III

Characteristics of dta curves of crude clays

Nature of peak	Peak temperature (per cent)	
	Padappa- kara	Kum- balam
Low temperature endothermic	102	100
Main endothermic	585	595
Main exothermic	985	975
Low temperature exothermic	460	—

TABLE IIIA

X-ray diffraction results of crude clays

Padappakara		Kumbalam	
d (Å)	I/I_1	d (Å)	I/I_1
7.25	10	7.25	10
4.50	8	4.50	8
4.40	4	4.40	4
4.30	4	4.30	4
3.54	9	3.54	9
3.34	8	3.34	8
3.10	2	3.10	2
3.00	4	3.00	4
2.55	7	2.55	7
2.475	7	2.475	7
2.45	4	2.45	4
2.323	8	2.325	8
2.275	7	2.275	7
2.225	W	2.225	W
2.15	W	2.15	VW
2.12	1	2.12	W
1.98	6VB	1.97	5VB
1.65	5VB	1.65	5VB
1.53	7	1.53	5
1.475	10B	1.475	10B
1.44	2	1.44	2
1.365	3B	1.365	2B
1.275	6B	1.275	6B
1.225	4B	1.225	4B
1.19	4B	1.19	4B
1.17	4B	1.17	4B
1.14	4B	1.14	4B

d —interplanar spacing; I/I_1 —intensity of line relative to the strongest as estimated visually; W—weak; B—broad; VB—very broad; VW—very weak

kara clay 90.8 per cent of particles existed below 2μ and Kumbalam clay contained about 87.2 per cent of particles finer than 2μ . The amount of particle finer than 0.5μ in processed Padappakara and crude Kumbalam were 82.0 per cent and 80.8 per cent respectively. It was, therefore, evident that the particles in both the clays were mostly in colloidal dimension.

The results of bec (Table IV) in me per 100 gm of clay obtained in case of these two clays showed very conclusively that both the two clays were very fine grained and further they also contained a very small quantity of organic humus fraction.

The plastic and dry properties of both crude and processed samples of the two clays are given in Table V. The plasticity of both Padappakara and Kumbalam clay was very good with high Atterberg's number and practically there

was no difference between crude and processed samples. The plasticity of the clays was remarkably high despite the large amount of free quartz present, particularly in crude Padappakara clay (21.63 per cent free quartz as obtained from rational analysis). This excellent plastic property could be attributed mainly to the extremely fine grain size (Table IV) of the clays. Water of plasticity of crude Padappakara clay was 44.3 per cent and the value remained almost the same even after processing.

The dry transverse strength of processed Padappakara clay and crude Kumbalam clay, both mixed up with 50 per cent nonplastic material were 26 kg/cm² and 21.2 kg/cm² respectively, which showed that the values were appreciably high. High dry strength implied good bonding power, and was thus a direct indication of the ability of the material to stand up to handling in the unfired state without breakage.

The fired properties of the two clays at 1250° and 1400° are given in Table VI. The data on fired properties included in the present investigation were limited to the minimum necessary to give useful information on the possible industrial utilisation of the clays. Fired colour, degree of vitrification as determined by visual examination, per cent water absorption, fired linear

shrinkage, tendency to crack and warp and PCE values (Tables VI and II) had been selected as the factors most characteristic of clays for ceramic bodies during firing.

The crude Padappakara clay when fired at 1250° was pale white with minute grey specks and at 1400° was pale cream with the specks changing to brown and becoming more promi-

TABLE IV
Particle size distribution, bec and pH value

Particles	Padappakara processed (per cent)	Kumbalam crude (per cent)
Coarser than 25 microns	0.0	0.0
Between 25 and 15 microns	0.8	6.2
" 15 and 10 "	0.9	1.6
" 10 and 8 "	0.8	0.2
" 8 and 5 "	2.3	1.0
" 5 and 3 "	3.6	2.8
" 3 and 2 "	0.8	1.0
" 2 and 1 "	2.6	5.2
" 1 and 0.5 "	6.2	1.2
Finer than 0.5 microns	82.0	80.8
Less than 2 "	90.8	87.2
<i>Bec (mc per 100 gm of clay)</i>		
(a) clay as such	7.44	
(b) after removal of organic matter	6.43	
<i>pH value</i>	6.55	4.08

TABLE V
Plastic and dry properties of crude and processed clays

Properties	Padappakara		Kumbalam	
	Crude	Processed	Crude	Processed
Plasticity by hand feel	Very good (sticky)	Very good (sticky)	Very good (sticky)	Very good (sticky)
Atterberg's number	45	45	50	50
Liquid limit	79.4	79.0	90.3	83.0
Plastic limit	34.7	34.0	40.6	33.4
Water of plasticity (per cent)	44.3	44.9	55.7	47.0
Dry colour	Greyish white	Light grey	Light grey	Light grey
Dry linear shrinkage (per cent)	8.0	8.0	10.7	6.6
Dry transverse strength (with 50 per cent quartz) kg/cm ²	—	26	21.2	—

TABLE VI

Fired properties of crude and processed clays

Properties	Padappakara		Kumbalam	
	Crude	Processed	Crude	Processed
<i>At cone 7 (1250°)</i>				
(i) Colour	Dull pale white full of minute grey specks	Dull white with- out specks	Dull with pale white minute grey specks	Dull white turning to very light grey without specks
(ii) Vitrification	none	fair	slight	high
(iii) Water absorption (per cent)	12.1*	2.6*	5.8*	2.9*
(iv) Linear shrinkage (per cent)	18.0*	21.6*	25.6*	22.0*
<i>At cone 14 (1400°)</i>				
(i) Colour	Pale cream full of brown specks	Dull white turning to very light grey	Dull white turning to very light grey with minute brown specks	Dull white turning to very light grey
(ii) Vitrification	fair	high	high	high
(iii) Water absorption (per cent)	6.9*	2.3*	3.9*	2.3*
(iv) Linear shrinkage (per cent)	20.0*	21.6*	25.8*	22.7*

*The test pieces either checked, cracked or warped in firing and figures, therefore, are only approximate

nent. The fired colour of crude Kumbalam clay at 1250° was exactly similar to that of crude Padappakara clay but at 1400°, it was dull white turning to very light grey and with prominent brown specks. These undesirable fired specks, as discussed earlier were mainly due to the presence of ferruginous grits in the crude clays seen from the results of wet sieve analysis (Table I).

Conclusions

Padappakara clay was found to be highly plastic and although containing free quartz and marcasite as non-clay minerals may be considered as a very good substitute for ball clay after suitable processing. The processing required for Padappakara clay was only simple levigation and, therefore, should not require any complicated technology.

Kumbalam clay was found to be equally plastic but comparatively free from the associated non-clay impurities. It may be used even in the crude form in some industries where

the fired colour is not of much relevance.

With respect to the whiteware industries, however, a simple sieving operation through a 150 mesh sieve was found to eliminate most of the speck forming contaminants from the clay.

Summary

Ceramic properties of two clays, *viz*, Padappakara and Kumbalam clays from Trivandrum district, Kerala, were studied. Kumbalam clay was comparatively free from the associated non-clay impurities. Padappakara clay contained free quartz and marcasite.

Padappakara and Kumbalam clays showed high plasticity. Padappakara clay could be a very good substitute for ball clay. Kumbalam clay may be used in the crude form where the fired colour is not much important.

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HYPERSENSITIVITY OF THE NEODYMIUM ABSORPTION SPECTRA IN LEAD BORATE GLASSES

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Introduction

Absorption spectra of neodymium doped coloured glasses showed slight dependence on the neighbouring ligands owing to the screening of 4f electrons by the outer $5s^2 5p^6$ electrons. The effect of the crystal field on the electronic configuration of these ions is relatively small; the spin orbit coupling is much more important¹.

Studies of neodymium²⁻⁷ in different borate, silicate, phosphate or germanate glass hosts showed that the positions of the absorption bands in all of the glasses were in the same wavelength region of Nd^{3+} ions in aqueous solutions. However, an increased resolution of the spectra showed more fine structures. Some of the bands showed marked splitting to

two component peaks and the splitting increased with the apparent increase in covalency of the Nd-ligand bond.

In the present work, the effects of lead borate glass host on the absorption spectra of Nd^{3+} ions and the possible coordination states of these ions in the glassy network were studied.

Experimental

Glasses were prepared from chemically pure grade materials. The boric oxide was introduced as boric acid, lead oxide as red lead or minium (Pb_3O_4). The divalent metal oxides were introduced in the form of their respective carbonates except zinc oxide which was introduced as such.

Glasses were melted in Pt-2 per cent Rh crucibles in electrically heated furnaces at 1100° for 4 hours. Neodymium oxide was

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added in amounts of 2 gm per 100 gm glass. The annealed glasses were ground and perfectly polished for spectrophotometric measurements by a Beckman DR spectrophotometer. The results were plotted as the molecular extinction coefficients of the particular wavelengths and were calculated as follows*:

$$E_M = \frac{OD}{M \times L}$$

where OD is the optical density of the particular wavelength of a sample of thickness L cm and M is the concentration of the rare earth metal in mole/1000 cm² of the glass.

Results

Effect of the composition of lead borate glasses: The compositions of the glasses studied varied from PbO 42.1 – B₂O₃ 57.9 (mole per cent) to PbO 63.9 – B₂O₃ 36.1 (mole per cent) containing 2 gm Nd₂O₃ per 100 gm glass (Table I). It was found that the molecular extinction coefficient of the bands of Nd doped lead borate glasses generally increased progressively with the increase in the content of lead oxide.

The band at 350 mμ showed triply splitted peaks with the increase of lead oxide and overlapping of the weak band at 400 mμ. With the increase of lead oxide content, the bands at 400 and 1100 mμ disappeared completely while the bands at 430 and 1800 mμ remained unresolved. The band which appeared at

470 mμ was splitted into two peaks at 460 and 480 mμ.

Effect of the divalent metal oxides: The studies on the effect of the divalent metal oxides were carried out by replacing 2, 5 or 10 wt per cent (1.4, 3.4 or 6.9 mole per cent) of PbO of the parent glass of the composition PbO 55.5–B₂O₃ 44.5 (mole per cent) containing 2 gm Nd₂O₃ per 100 gm glass by magnesia, zinc oxide, cadmium oxide, lime, strontium oxide or barium oxide (Table II). It was observed that (i) the intensities of the absorption bands increased to a very small extent with the increase of ZnO content, although the band at 350 mμ decreased with the increase of the same, (ii) generally the intensities of the magnesia or cadmium oxide containing glasses were closely similar but less than that of the corresponding ZnO containing glasses, (iii) the intensities of the bands increased with the increase of BaO content in the glass, (iv) the intensities of the bands of CaO or SrO containing glasses were less than that of the corresponding BaO containing glasses, (v) the intensities of the bands progressively decreased with the increase of CaO or SrO content, and (vi) the addition of the divalent metal oxides to the lead borate glasses caused marked splitting of the band centered at 350 mμ.

Discussion

NMR^{9,10} and IR studies¹¹ indicated that the fraction of N₄ of four-coordinated boron atoms in lead borate glasses increased with the increase of the lead oxide content until about 50 mole per cent PbO and then decreased again. Increasing PbO content beyond this limit caused disruption on the glassy network and it was expected that a part of the lead ions existed as PbO₄ groups while the remaining Pb²⁺ ions could be housed in the interstices of the glass structure¹². The two outer electrons of the Pb²⁺ ion were easily repelled by the field of negative oxygen ion. As a result, the Pb²⁺ ion lost its spherical symmetry and its electron distribution was such that towards

TABLE I

Compositions of lead borate glasses containing 2 gm Nd₂O₃ per 100 gm glass. Each glass was melted for 4 hours at 1100°

Glass	Composition (mole per cent)		Composition (wt per cent)	
	PbO	B ₂ O ₃	PbO	B ₂ O ₃
95	42.1	57.9	70	30
96	48.4	51.6	75	25
97	55.5	44.5	80	20
98	63.9	36.1	85	15

TABLE II

Compositions of lead borate glasses containing 2 gm Nd_2O_3 per 100 gm glass. Each glass was melted for 4 hours at 1100°

Glass	Composition (mole per cent)			Composition (wt per cent)		
	PbO	B_2O_3	RO	PbO	B_2O_3	RO
99	54.1	44.5	1.4 MgO	78	20 MgO	2 „
100	52.1	44.5	3.4 „	75	20 „	5 „
101	48.6	44.5	6.9 „	70	20 „	10 „
102	54.1	44.5	1.4 ZnO	78	20 ZnO	2 „
103	52.1	44.5	3.4 „	75	20 „	5 „
104	48.6	44.5	6.9 „	70	20 „	10 „
105	54.1	44.5	1.4 CdO	78	20 CdO	2 „
106	52.1	44.5	3.4 „	75	20 „	5 „
107	48.6	44.5	6.9 „	70	20 „	10 „
108	54.1	44.5	1.4 CaO	78	20 CaO	2 „
109	52.1	44.5	3.4 „	75	20 „	5 „
110	48.6	44.5	6.9 „	70	20 „	10 „
111	54.1	44.5	1.4 SrO	78	20 SrO	2 „
112	52.1	44.5	3.4 „	75	20 „	2 „
113	48.6	44.5	6.9 „	70	20 „	10 „
114	54.1	44.5	1.4 BaO	78	20 BaO	2 „
115	52.1	44.5	3.4 „	75	20 „	5 „
116	48.6	44.5	6.9 „	70	20 „	10 „

the O^{2-} ions it extended only its 18-electrons of the O-shell, which meant that it assumed the electron distribution of much smaller and highly charged Pb^{4+} ion.

Introducing lead ions with big charges and radii lead to a weaker ligand field and great resolution of the 4f band structure. This explained the greater increase of the molecular extinction coefficients of the bands maxima. As a result the bands maxima shifted to shorter wavelengths with a marked increase in the molecular extinction coefficient. The gradual shift to longer wavelengths of the absorption curves, may, in some way, be related to the very strong absorption in the ultraviolet region of glasses containing lead oxide.

Effect of the divalent metal oxides: The effect of introducing divalent metal oxides in lead borate glasses was expected to depend on: (i) the type, coordination number and quantity

of the introduced oxide; (ii) the formation of new structural building units such as MgO_4 , ZnO_4 or CdO_4 ; and (iii) the degree of covalency in bonding of the divalent metal to oxygen.

The relative effect of these divalent oxides was attributed to the degree of the polarisability of the oxygen ligands. With further increase of divalent metal oxides, the equilibrium between the nine- and six-coordination shifted probably towards the coordination state.

The decrease in the molecular extinction coefficient with increase in the divalent oxide content might be due to the decrease in the basicity of these glasses. The decrease in the basicity may result, as mentioned in the theoretical concentration of divalent metal oxides in lead borate glasses, from the decrease in the number of the BO_4 groups. The basicity decreased in the order $\text{Cd} > \text{Zn} > \text{Mg}$ and

Ba > Sr > Ca which was in good agreement with the experimental results of the glasses containing neodymium.

Summary

Molecular extinction coefficient of the absorption bands of Nd doped lead borate glasses increased progressively with the increase in the content of lead oxide. Increase in lead oxide content resulted in triply splitted peaks

of the band at 350 m μ and overlapping of the weak band at 400 m μ . With further increase in the content of lead oxide, the bands at 400 and 1100 m μ disappeared completely while the bands at 430 and 1800 m μ remained unresolved. The band which appeared at 470 m μ was splitted into two peaks at 460 and 480 m μ . Addition of divalent metal oxides caused marked splitting of the band around 350 m μ .

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THERMAL EXPANSION STUDIES ON GLASSES OF THE SYSTEM $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$

N. A. GHONEIM*

Introduction

Thermal expansion of glass from its chemical composition was first made by A. Winkelmann and O. Schott¹. They proposed a simple additive relationship between the property of glass and the nature and amounts of constituents present, *ie*,

$$P = \sum P_1 W_1 \quad \dots (1)$$

where P is the property, P_1 is a constant for the oxide present in the glass and W_1 is the weight fraction of the oxide.

Different authors²⁻⁵ proposed different factors for the calculation of the coefficient of thermal expansion but none of the equations introduced were found to be valid for all types of glasses.

The additive equation introduced by P. K. Gupta and S. Kumar⁶ is as follows:

$$\alpha = \sum a_1 c_1 \quad \dots (2)$$

where α is the coefficient of linear thermal expansion of glass between room temperature to 100° and c_1 is the concentration of the 'i'th oxide in gm per cc of glass and a_1 is a constant for the 'i'th component, *ie*,

$$\alpha = d \sum a_1 w_1 \quad \dots (3)$$

where w_1 is the weight fraction of the 'i'th oxide present in the composition and d is the density of the glass.

In spite of few limitations, such as the presence of some glass forming ions as Al^{3+} and

B^{3+} in two states of coordination in glass structure, the equation was found to be very satisfactorily applied.

In observing the thermal behaviour of glass, no characteristic melting point was available and particular points were proposed to replace this constant value. The present study was undertaken to differentiate between the Littleton softening point⁷ (M_g) and the maximum point reached on the thermal expansion curve for the glass (T_g).

G. W. Morey⁸ considered that the effect observed at the transformation point T_g had been caused by the failure of the glass to reach internal equilibrium at lower temperature with the result that, when the viscosity was sufficiently diminished by heating, the frozen-in lag was suddenly released.

R. W. Douglas and G. A. Jones⁹ suggested that the apparent transformation point, observed in any typical measurement of the thermal expansion of the glass, had no real existence. It was the temperature at which, in the particular experiment considered, the rate of approach to equilibrium configuration became comparable with the time required to make an observation.

The aim of this work was to clarify the dilatometric thermal properties of glasses based on the $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ system. Cation replacements of parts or all of the lime by monovalent or divalent metal oxides to reevaluate the validity of the recent interpretations and the additive equation considering the published softening point results on the same glasses.

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Experimental

All glasses (Tables I and II) were prepared from AR grade pure chemicals. Alkali oxides, lime, MgO, SrO and BaO were introduced as their respective carbonates. Al_2O_3 and ZnO were added as such. B_2O_3 was added as boric acid.

The glasses were melted in platinum-2 per

cent rhodium crucibles in electrically heated furnaces at 1350° for four hours.

Glass specimens in the form of rods approximately $5 \times 5 \times 50$ mm were used after heat-treating in a muffle furnace at 450 – 550° and subsequently cooling down slowly to room temperature. The initial length was measured by micrometer to the nearest 0.001 cm.

TABLE I

Variation of T_g , M_g and coefficient of thermal expansion of the glasses CaO 30, B_2O_3 40 and Al_2O_3 30 wt per cent with partial or total replacement of lime by monovalent alkali cations

Glass	Glass composition (wt per cent)				α_{50-300} ($\times 10^{-6}/^\circ\text{C}$)	T_g ($^\circ\text{C}$) (transformation temperature)	M_g ($^\circ\text{C}$) (softening point)
	CaO	B_2O_3	Al_2O_3				
					6.00	598	688
2	29	40	30 Li_2O	1 CaO	6.23	590	693
3	25	40	30 „	5 „	6.56	569	667
4	20	40	30 „	10 „	7.24	541	641
5	15	40	30 „	15 „	8.03	519	620
6	10	40	30 „	20 „	8.91	490	588
7	5	40	30 „	25 „	9.42	461	561
8	—	40	30 „	30 „	10.67	449	550
9	29	40	30 Na_2O	1 „	6.18	592	694
10	25	40	30 „	5 „	6.43	576	673
11	20	40	30 „	10 „	7.19	550	648
12	15	40	30 „	15 „	7.89	523	627
13	10	40	30 „	20 „	8.44	501	593
14	5	40	30 „	25 „	9.03	480	566
15	—	40	30 „	30 „	10.02	455	555
16	29	40	30 K_2O	1 „	6.12	594	694
17	25	40	30 „	5 „	6.36	586	680
18	20	40	30 „	10 „	7.04	554	651
19	15	40	30 „	15 „	7.61	530	634
20	10	40	30 „	20 „	8.19	505	598
21	5	40	30 „	25 „	8.68	487	569
22	—	40	30 „	30 „	9.29	458	559

TABLE II

Variation of T_g , M_g and coefficient of thermal expansion of the glasses CaO 30, B_2O_3 40 and Al_2O_3 30 wt per cent with partial or total replacement of lime by divalent metal oxides

Glass	Glass composition (wt per cent)				α_{70-300} ($\times 10^{-6}/^\circ\text{C}$)	T_g ($^\circ\text{C}$) (transformation temperature)	M_g ($^\circ\text{C}$) (softening point)
	CaO	B_2O_3	Al_2O_3				
23	29	40	30 MgO	1 CaO	5.92	606	692
24	25	40	30 „	5 „	5.80	613	698
25	20	40	30 „	10 „	5.59	621	705
26	15	40	30 „	15 „	5.28	630	711
27	10	40	30 „	20 „	5.00	633	718
28	5	40	30 „	25 „	4.77	635	725
29	—	40	30 „	30 „	4.15	637	735
30	29	40	30 ZnO	1 „	5.92	602	692
31	25	40	30 „	5 „	5.83	609	697
32	20	40	30 „	10 „	5.66	612	703
33	15	40	30 „	15 „	5.48	620	708
34	29	40	30 ClO	1 „	6.10	597	683
35	25	40	30 „	5 „	6.25	593	674
36	20	40	30 „	10 „	6.51	528	666
37	15	40	30 „	15 „	6.78	572	657
38	10	40	30 „	20 „	7.00	564	648
39	5	40	30 „	25 „	7.23	559	638
40	—	40	30 „	30 „	7.40	554	627
41	29	40	30 SrO	1 „	6.10	597	682
42	25	40	30 „	5 „	6.28	591	673
43	20	40	30 „	10 „	6.60	580	664
44	15	40	30 „	15 „	6.94	573	652
45	10	40	30 „	20 „	7.28	561	683
46	5	40	30 „	25 „	7.33	553	630
47	—	40	30 „	30 „	7.85	546	620
48	29	40	30 BaO	1 „	6.17	594	682
49	25	40	30 „	5 „	6.30	584	672
50	20	40	30 „	10 „	6.68	570	662
51	15	40	30 „	15 „	7.01	558	650
52	10	40	30 „	20 „	7.41	541	635
53	5	40	30 „	25 „	7.89	530	625
54	—	40	30 „	30 „	8.41	512	615

Linear thermal expansion coefficients were determined by automatically recording Linseis dilatometer. The specimen holder and extension rod used were made of fused quartz. The thermal expansion was measured by a differential method in which the expansion of the glass rod was compared with that of a fused silica rod. Temperature readings were made with a platinum-rhodium thermocouple placed directly on the specimen.

Millivoltmeter readings were plotted against change in length with an X-Y recorder with a speed of 60 mm/hour. After measuring the initial length, the rod was put at the centre of the fused silica assembly and before proceeding with the measurement, the sample was first heated to very close to its softening point and then cooled at less than 2°/minute. The heating rate in all cases was 5°/minute.

The data was checked for accuracy by measuring another rods with similar dimensions by a horizontal dilatometer of a dial gauge assembly with steps of 0.0001 inch. The heating rate was controlled by a suitable energy regulator. The same rate of heating as used before was repeated and comparable results were obtained.

The coefficient of linear thermal expansion was calculated as follows:

$$\alpha \times 10^{-6} = \frac{A}{L \Delta T V} + 0.5$$

where A is the extension measured, L is the initial length of the glass specimen, ΔT is the difference in the temperature range, V is the value expressing the sensitivity of the dilatometer, and 0.5 is a constant of quartz system.

Results and discussion

The mean linear thermal expansion coefficients between 50° and 300° for all glasses measured are summarised in Tables I and II. Thermal expansion curves representative of all glasses in the system CaO-B₂O₃-Al₂O₃ are shown in Fig 1. A slight curvature was apparent especially above 300° with a change of slope (a 'Kink')¹⁰⁻¹² at this temperature. A very marked

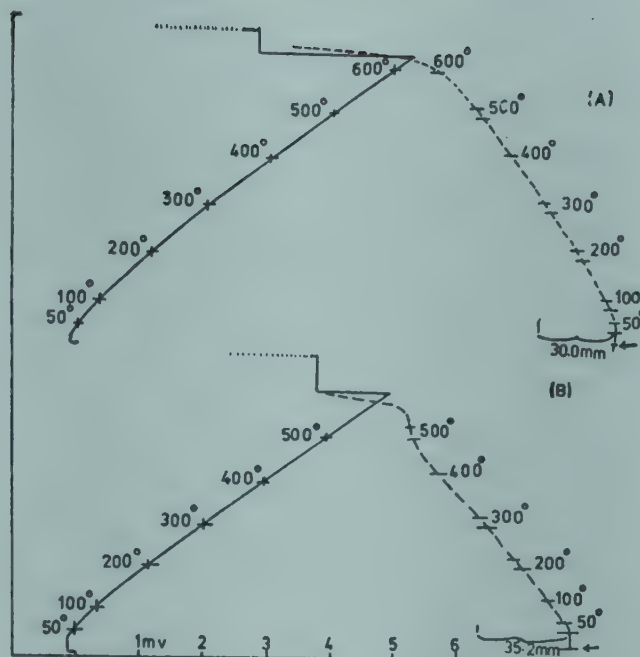


Fig 1

Dilatometric expansion curves: (A) well annealed glass;
(B) unannealed glass

curvature was observed at the region between the 'dilatometric transformation temperature T_g ' and the 'softening temperature M_g '.

Coefficient of thermal expansion of glasses increased with the increase of alkali oxide that replaced lime (Table I). The coefficient of thermal expansion decreased with increasing cation size, in the order $Li > K$.

The transition temperature T_g varied with the change in the glass composition in the same way as Littleton softening temperatures with the same glass compositions¹³.

The coefficient of thermal expansion of the glasses, containing parts or all of the lime substituted by one of the divalent metal oxides, ie, MgO, ZnO, SrO, BaO or CdO are shown in Table II. A decrease in the coefficient was observed with glasses containing magnesia or zinc oxide while the other remaining oxides produced higher coefficient of thermal expansion. The transition temperatures T_g showed a reverse trend to the increase or decrease of the coefficients to each respective divalent metal oxide.

The replacement of the divalent cation Ca^{2+} by any of the monovalent alkali cations (Li^+ , Na^+ , K^+) could be assumed to bring structural changes in the glassy network. The alkali metal cations will eventually occupy positions different¹⁴ from those of the Ca^{2+} cation. Some of the bridging O^{2-} ions would be changed to non-bridging O^{2-} ions. The structural building units would therefore, participate with O^{2-} ions tightened to different cations. As a result of such inharmonicity of the $\text{M}^{3+}\text{-O}$ bonds, the resultant groups would be asymmetric¹⁵. The asymmetry of the building units would be more in the presence of the high polarisable non-bridging O^{2-} ions, *ie*, in the presence of K^+ cations than in the presence of Li^+ cations. This view is in good agreement with the results obtained by L. Shartsis, S. Spinner and W. Capps¹⁶. W. A. Weyl¹⁷ assumed that expansivity should increase with increasing polarisation of the ion.

With the increase of alkali oxide content in aluminoborate glasses the network will assume a looser structure and hence the coefficient of thermal expansion is expected to decrease¹⁹.

In the glasses studied, the alkali ions are the most weakly bonded constituents, and as a result, they will be able to move easily (or become more mobile) through the building units. Increasing the glass temperature up to T_g increases the movement of the constituent ions. As a result of such mobility they can move away from the non-bridging O^{2-} ions, and interact with the neighbouring bridging O^{2-} ions and contrapolarise it. This would weaken the $\text{M}^{3+}\text{-O}$ bonds more than one would expect from the increase in thermal vibration.

At higher temperatures, the change of positions between the bridging and non-bridging oxygen ions becomes more pronounced, the O^{2-} ions become sufficiently mobile and can move within the anion network and diffusion through the bulk is possible. This may also explain the sudden change in the coefficient of thermal expansion at T_g observed in the dilatometric thermal curves.

D. R. Uhlmann and R. R. Shaw¹⁹ observed

the effect of replacing Ca^{2+} ions by the divalent metal oxides. In the case of properties which are highly sensitive to structural cohesiveness, the smaller cations with higher field strengths seem to produce more strongly bound structures than the larger cations, and the smaller cation glasses are generally characterised by larger moduli, smaller expansion coefficients *etc.* Also the possibility arises that some of the divalent metal cations (Mg^{2+} , Zn^{2+}) can participate in the glass structure and form network forming tetrahedral units. The vibration of these groups are not so easy as if the cations are in interstitial positions and hence the observed increase in the transformation temperatures of the glasses containing any of these two cations.

The expansion coefficient of glasses could be partly related to the bond strengths between the cations and the oxygen ions¹⁸.

The main factors which affected the values of the transformation temperature are: (a) the mobility of the constituent ions and ease of thermal vibration, (b) the screening of the cations, and (c) the repulsion between the cations which depends on the polarisation of both cations and anions present, their field strengths as well as their charges.

Thermal expansion of certain crystals also depends on the thermal rotation of the structural groups or angular movements involving changing in the bond angles. Such effects are not possible due to randomness in its structure.

Summary

Thermal expansion studies on glasses of the system $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ with some cation replacements were carried out by differential dilatometric measurements.

The change in coefficient of expansion of the glass with the increase of added oxide content was discussed in relation to the mode of vibration of the atoms (or groups) in the network, the polarisation of the ions, the mobility of the constituent ions and the ability of some cations to build glass forming units.

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